METALLURGICAL PROCESS ENGINEERING

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PREFACE

The engineering of metallurgical processes is presently in a high state of flux. The advent of the high speed computing machine has been a tremendous stimulus in promoting a re-examination of process design procedures. In this regard, it has been recognized by most educators in the field of extractive metallurgy that a unit process treatment of the subject has much more to offer in its analytical approach than a descriptive presentation of current practice. This text is based on the unit process concept, and attempts to extend it to a consideration of the design of entire extractive processing systems.

The future of metallurgical process engineering will undoubtedly involve, in addition to the advances in metallurgical science, techniques which are adopted from chemical engineering, instrumentation, computing, economics, operations research, and other allied fields. The metallurgical engineer should be acquainted with these areas, at least to the point of being able to evaluate possible contributions to metallurgical processing operations by specialists from these fields. Ideally, in a metallurgically oriented organization, the trained metallurgist should be prepared to assume a position of leadership in the engineering team which handles the many-faceted problems of metallurgical process design and operation.

This book reflects an effort to expand the teaching emphasis in extractive metallurgy, and includes an introduction to some of the fields which are important in metallurgical process design and operation. Every effort has been made to develop an analytical approach to the engineering of metallurgical unit processes. In addition, the text includes introductory material on the use of computers in process engineering, operations research procedures which treat system behavior in terms of queueing theory or linear programming models, as well as the mathematical simulation of processing systems, and consideration of the engineering of integrated systems.

The experience of teaching a course entitled, "Metallurgical Process Design", to juniors and seniors at the University of Michigan has provided the material for this publication. This course is preceded by courses in Process Stoichiometry, Chemical Engineering Thermodynamics, and Rate Operations which involve 3, 4, and 4 semester hours, respectively. This preparation and a one hour required course in digital computer programming is an excellent one for the present subject. Consequently, only a brief review of stoichiometry, thermodynamics and kinetics in the first chapters has been included. Furthermore, a knowledge of heat transfer and fluid flow on the part of the student has been assumed. In the event that additional reading in these areas is necessary, "Unit Operations" by A. S. Foust and "Heat Transmission" by W. H. McAdams are excellent reference texts.

In view of the fact that the presentation is primarily analytical, it is necessary that it be supplemented by descriptive material to provide the student with a clearer understanding of the environment in which the processes under consideration operate. The principal use of the descriptive material should be in consideration of metallurgical processing systems, following a development of the unit process approach. C. R. Hayward's "Outline of Metallurgical Practice", J. Newton's "Extractive Metallurgy", or the texts on nonferrous and ferrous production metallurgy by J. L. Bray are possible sources of this material. In addition, the references from the technical literature at the end of each chapter provide an excellent source of descriptive material.

The integration of example problems, both for classroom use and homework, is a vital part of the presentation of this material. The text itself contains only a few such problems, although a supplementary problem set is presently under development. Thus it becomes the responsibility of the instructor to provide additional material which will develop the student's engineering judgement and analytical approach to design problems. "Metallurgical Problems" by Allison Butts is a possible source of additional problems.

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TABLE OF CONTENTS

PART I Foundations of Metallurgical Design

PART II Materials Preparation, Treating, and Handling

PART III Primary Metal Production

PART IV Refining Operations

PART V Integrated Operations

LIST OF TABLES

LIST OF TABLES (CONT'D)

LIST OF FIGURES

Figure Page

Part I

Part II

LIST OF FIGURES (CONT'D)

LIST OF FIGURES (CONT'D)

Part V

Part I

FOUNDATIONS OF METALLURGICAL DESIGN

CHAPTER I

INTRODUCTION

A treatment of the science and of the art of process metallurgical engineering may be approached in two ways. The first, and one which has been highly popular in past years, is that of treating the extraction and processing of each individual metallic element starting with the mined ore and ending with a semi-finished product. The second approach, and one which has become necessary in view of the constantly expanding frontiers of metallurgy and the diversity of processing systems used in metallurgical industries, recognizes that each of these processing systems is made up of a number of unit operations and processes which possess general similarities independent of the material being processed.

The terms, unit operations and unit processes, were first used by chemical engineers to designate the unit actions in the manufacturing processes of the chemical industry. A distinction may be made between unit operations and unit processes on the basis of whether or not the process involves physical or chemical changes. Unit processes are defined as those operations which involve chemical reactions and/or changes in state of aggregation while unit operations primarily do not involve either bulk reactions or changes in state. ~~Metallurgical~~ unit operations would include screening, size reduction, handling of solids and fluids, classification, flotation, sedimentation, and other material separation processes. Metallurgical unit processes would include such gas-solid processes as roasting, calcining, and gaseous reduction. They would include as well, sintering, the reduction of oxides, smelting operations, converting, refining, hydrometallurgical processes, electrolytic processes, and other metallurgical operations which involve chemical reactions or changes in state. This text is devoted to the development of an engineering approach to the design and integration of metallurgical unit processes.

It should be noted that there is a distinct need for several kinds of unit operations and unit processes in sequence. This need arises from the fact that no single unit operation or process is capable of separating a metal from all of the elements associated with it. Consequently, a coordinated sequence of operations and processes is made up such that materials flow from one step to the next in an orderly fashion. These integrated processes may make up the entire plant or section of a plant in which the metal is being processed. Successful operation of an industrial process requires intimate knowledge of the relations of the large-scale process to its surroundings and careful coordination of those relations with each other and with the internal characteristics of the process.

The engineer who has a sound foundation in the principles of metallurgical operations; i.e., in stoichiometry, fluid flow, and heat transfer, as well as a good background in thermodynamics and kinetics, should be able to apply this knowledge and readily adopt himself to the mathematical analyses and practical applications of metallurgical unit processes. The material presented in this test assumes such a background, although the first section has been devoted to reviewing a part of that material. The goal here is not only an understanding of unit processes, but a preparation for an even more advanced state of metallurgical process design, the engineering and design of metallurgical processing systems.

In recent years, the processing industries have come to realize more and more that they can no longer think of their plants as an assemblage of individual units. It is becoming apparent that each of the separate units in a processing system influences the others in many subtle ways as well as the more obvious, direct ones. The principles of feedback systems have been recognized for some time, but little has been done to implement these principles for the purpose of process control. Recent advances in the mathematical treatments of integrated systems coupled with a better appreciation for the interaction of units making up a system, have led to a new engineering technique, that of system engineering. System engineering strives to optimize the operation of entire plants or systems contained within them, and prepares to do so by analyzing the operation of each of the individual units and integrating the analyses of them.

The advent of system engineering is undoubtedly the dawning of a new era in process engineering. This advance represents a challenge to the metallurgical engineer. The meeting of this challenge is the goal to which this text is committed.

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CHAPTER II

STOICHIOMETRY - MASS AND ENERGY BALANCES

The basis of engineering analyses of metallurgical processes is the mass and energy balances which may be set up for a process. The stoichiometric relations which make up these mass and energy balances are in themselves quite simple. They could be summarized by the old observation, "What goes in, must come out!", or more precisely as, the input to a system is equal to the output from the system plus any accumulation within the system. This statement is based on the assumption that matter is neither created nor destroyed, and also that matter and energy are not interchangable. This assumption is contrary to the foundations of nuclear science, but is one of general validity in metallurgical process operations.

Processes may be divided into two classes, batch and continuous. In the batch process the charge materials are placed in a tank or container and then permitted to react by interchange of materials between the charge streams or the interchange of energy between the charge materials themselves or between the container and the charge materials. When the charge of the batch process has reached the desired conditions, it is removed and new charge materials are placed in the container. In the continuous process the charge materials are passed continuously through the container, the reacting volume and the rate of flow being adjusted so that the materials leave the system at the desired conditions.

Each of these classes of processes has certain advantages and the choice of the process to be used is the responsibility of the engineer. The batch process generally involves equipment which is simpler and easier to fabricate. It does not require as close control and the control is needed only toward the end of the process. The batch process is intermittent, and consequently, associated with such a process are the problems of storage facilities to absorb the fluctuations in the rates of production.

The continuous process, generally requiring more carefully designed equipment than the batch process, can usually be handled in a smaller space and with continuous operation which easily fits into a smooth flow of production through the plant. The temperature in each part of the continuous process equipment will remain substantially constant during the operation. Thus the continuous operation has an advantage from the point of engineering design. Conditions will be different at different points in the continuous system, but will remain constant at each particular point. This is called a steady state process and is in many respects an ideal one. The mathematical treatment of the steady state process is generally much easier than that for a non-steady state process. The continuous process does involve non-steady state conditions, however, during startup and shutdown periods, but throughout the course of operation, the continuous process is in what may be described as a steady state condition.

Mass Balances

The materials balance for an unsteady system was stated previously:

$$\text{Input} = \text{Output} + \text{Accumulation} \qquad \text{II-1}$$

A steady system, however, will contain a fixed and unvarying quantity of any given element so that the balance simplifies to:

$$\text{Input} = \text{Output} \qquad \text{II-2}$$

This simpler relation also applies to batch processes and other unsteady systems if the input and output are measured for period of time such that the system is in the same condition at the beginning and the end of that period.

For the process shown in Figure II-1, the over-all material balance may be stated mathematically as:

$$a_1 + a_2 = b_1 + b_2 \qquad \text{II-3}$$

where a_1 = total mass of stream A_1, a_2 = total mass of stream A_2, b_1 = total mass of stream B_1, b_2 = total mass of stream B_2.

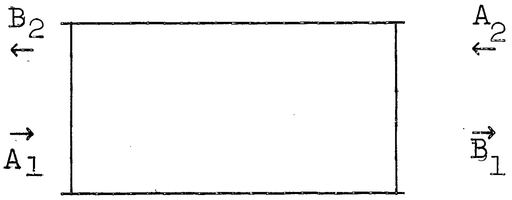

Figure II-1 Process Flow Diagram

If the process is a batch process the mass of the streams may be expressed in weight units. If, however, the process is a continuous one, rate of flow may be used, expressed as mass per unit time.

In the case where the reactions taking place in a process are purely physical, the material balance may be written for each material involved. If, however, a chemical reaction is taking place, the balance must be written in the form of an element balance. The principle of conservation of elements may be used. This principle states that matter is composed of atoms which are unchanged during the course of a chemical reaction. Furthermore, this principle may be extended to state that when atoms combine to form molecules, these combinations are brought about such that the weight of the molecule is precisely equal to the sum of the weights of the atoms which make it up.

In addition to the principle of conservation of elements, the ideal gas law is also an important consideration, especially since gas phases are involved in nearly all process operations. Boyle's law states that at constant pressure, the volume of a given mass of gas is inversely proportional to the pressure. Charles' law states that at constant pressure the volume is proportional to the absolute temperature. These statements are strictly true only for an ideal gas and lead to the ideal gas law. The relationship for an ideal gas is thus:

$$PV = NRT \qquad \text{II-4}$$

where P = pressure, V = volume, N = number of moles of gas, R = gas constant, and T = absolute temperature. Real gases closely approach the ideal behavior represented by the above equation at low pressures and high temperatures. Since these are the conditions under which most metallurgical systems operate, no significant errors are introduced by assuming ideal behavior for gases involved in nearly all metallurgical operations.

The law of combining volumes follows from the ideal gas law and affords a further simplification of engineering calculations. According to this principle, the volume of a mixture of two gases is equal to the sum of the volumes of the individual gases, and the volume fraction as well as the mole fraction are given by the partial pressure of one gas divided by the total pressure of the gas mixture.

When complete and accurate stoichiometric data are available for a process, a table is easily drawn up to show the balances for the materials and for each important element. A typical metallurgical balance is presented in Table II-1.

In principle, all of the quantities entering and leaving a process with no accumulation or loss can be calculated if complete analyses on all streams and the quantity of one of the materials in each stream are known. Simultaneous equations can be solved for the unknown quantities which may be either weights or analyses of streams. If N independent element balances can be written, N unknowns can be solved for. If there are more independent equations than there are unknowns, several sets of answers can be calculated and checked against each other. Solutions of simultaneous equations set up from practical data are often in error because small errors in the original data can greatly be magnified in the solution. Even negative answers may be obtained and such results are often due to the fact that solutions are obtained by a method of difference, and large errors may arise in solving the equations where a small quantity is determined by the difference between two large quantities. The engineer must be aware of this difficulty, as well as be able to recognize and avoid it.

It is rarely necessary to formally set up and solve a list of simultaneous equations involving all of the elements. Examination of the problem will usually reveal a simpler procedure for solving the particular problem. One factor which may be of assistance can arise from the fact that one element may enter and leave the process in a stream unchanged. For example, nitrogen often acts as an inert material which enters as air and leaves in the gaseous product. If the percentage of nitrogen in the exit gas is available and either the volume of

TABLE II-1 Metallurgical Balance for Dwight-Lloyd Sintering Machine

Basis: Per 1000 lb. of dry charge

FEED		PRODUCT			
Charge - lb		Sinter - lb		Gases(suction box)-lb	
Lead Ore (645):					
PbS	387	Pb	335	S	52
FeS_2	26	Fe	12	S	14
SiO_2	232	SiO_2	232		
Silver Ore (65):					
PbS	3	Pb	3	S	0
Ag_2S	0.3	Ag	0.3	S	0
SiO_2	61.7	SiO_2	61.7		
Spathic Iron Ore (129)					
$FeCO_3$	129	FeO	80	CO_2	49
Limestone (161):					
$CaCO_3$	161	$CaCO_3$	80.5	CO_2	35.5
		CaO	45		
Moisture (100):					
H_2O	100			H_2O	100
Oil (5)					
C	4.3			C	4.3
H	0.7			H	0.7
Air (774)					
N	595			N	595
O	179	O	31	O	148
Total	1879		880.5		998.5

From: A. Butts, *Metallurgical Problems*, McGraw-Hill Book Co. New York, 1943, p. 231.

air or of the exit gas is also available, the other volume is readily calculated without regard for other stoichiometric data on the process.

A general procedure should be adopted for setting up and solving the mass balances around metallurgical processes. Such problems are rarely difficult, but are generally long and tedious and offer many opportunities for arithmetic and other errors which are not easy to find and correct. Hence, from the very start a logical procedure of problem solving should be adopted, clearly writing out all steps so the solution can be quickly retraced and checked by another person if necessary. The procedure should include a simple line drawing of the system with indicating arrows showing the direction of each stream, the known stoichiometric data, and the assumptions which are valid for the process and which may serve as a basis for solution, the basis for the calculation, and the balanced chemical equations which will account for specific compounds or elements. Once this has been done, the equations may be inspected and a procedure decided upon for the solution of the problem. The solution should then be carried out and the results tabulated in a metallurgical balance table. The solution should finally be checked to see that all conditions are fulfilled and that the required results have been obtained.

Energy Balances

All processes involve the interchange of various kinds of energy with the surroundings. In most metallurgical processes, heat energy is the principal form of energy exchanged between the metallurgical system and its surroundings. The supply and utilization of heat range in importance with the supply and utilization of raw materials in determining costs and thus the success or failure of a process. For example, the availability of fuel or of low cost power has in many cases been the primary factor in the choice of plant location. Hence, the system of energy accounting or an energy balance for the process showing input and output of heat and other forms of energy is one of the indispensable tools that the metallurgical engineer uses. Just as the principle of conservation of elements afforded a simple approach to the materials balance, the principle of conservation of energy or the first law of thermodynamics affords a sound basis for setting up an energy balance. In both cases, a complete accounting of what goes into and what comes out of the system is made with little concern for the reaction mechanisms which operate within the system during the process operation.

The first law of thermodynamics may be written as:

$$\Delta E = Q - W \qquad \text{II-5}$$

where ΔE is the energy change of the system, Q is the heat absorbed by the system from the surroundings, and W is the work done by the system on the surroundings.

The heat content or enthalpy of the system, H is the thermodynamic property defined as:

$$H = E + PV \qquad \text{II-6}$$

where E is the energy content of the system, P is the pressure, and V the volume of the system. Combining with the previous equation, the first law may be written as:

$$H_2 - H_1 = Q - W + P_2V_2 - P_1V_1 \qquad \text{II-7}$$

For a constant pressure process, in which all the work done by the system on the surroundings is the work of expansion, that is, the integral from $1 \rightarrow 2$ of PV, $P_2 = P_1 = P$ and $W = P(V_2 - V_1)$. Combining the two equations above, $H_2 - H_1 = Q_p$ or $\Delta H = Q_p$, where Q_p is the heat absorbed by the system in changing from state 1 to state 2 by path of constant pressure in which only expansion work is done on the surroundings.

If the change in state is at constant pressure, but involves work other than expansion work on the surroundings,

$$\Delta H = Q_p - W' \qquad \text{II-8}$$

where W' is the work done by the system on the surroundings in the constant pressure process, but does not include expansion work. For example, in an electric furnace process at constant pressure, -W' = the input of electrical work to the system. Since most metallurgical processes follow paths of substantially constant pressure, the previous equation is a very useful one.

Before introducing the energy balance itself, it would be best to first discuss the principles of thermochemistry which underlie the various aspects of that balance. Thermochemistry is a branch of science which is concerned with energy changes, usually in the form of heat which accompany chemical reactions. Thermochemistry as a science can be summarized by several laws which form the basis for most of the calculations accompanying heat effects in chemical reactions. In 1780 Lavoisier and LaPlace stated that the heat evolved in a given reaction is equal to the heat absorbed in the reverse reaction. This law is merely an expression of the more general law of conservation of energy. In 1840, Hess, in his law of constant heat summation, stated that the heat of a chemical reaction at constant pressure is independent of the number of intermediate steps involved. In other words, the total change in enthalpy of a system is dependent upon only the initial and final conditions of the system and is independent of the number of intermediate chemical reactions involved.

Systematic thermochemical data are readily available for the following simple thermodynamic changes in state, all at constant pressure:

1. temperature changes in pure substances
2. changes in state for pure substances
3. formation of compounds from elements
4. formation of solutions.

The variation of heat content with temperature is expressed for most substances by a number of empirical relations involving temperatures to various powers. The quantity calculated is not the absolute heat content, but the relative heat content, $H_t - H_{298}$. The temperature 298°K or 25°C is known as the base temperature and the quantity $(H_t - H_{298})$ is then the heat content above the base temperature. The variation in the sensible heat with temperature is called the heat capacity c_p which is defined as:

$$c_p = \left[\frac{\partial H}{\partial T} \right]_p \qquad \text{II-9}$$

Integration of the above equation gives:

$$H_2 - H_1 = \int_{T_1}^{T_2} c_p \, dT \qquad \text{II-10}$$

Values of the sensible heat are tabulated in various sources.

After a solid is heated to its melting point, additional heat must be supplied to melt it. The heat required for melting at constant pressure is equal to the increase in heat content from the solid to the liquid and is known as the heat of fusion. An equal quantity of heat is liberated during solidification, so that

$$\Delta H \text{ solidification} = -\Delta H \text{ fusion} \qquad \text{II-11}$$

Similarly, heat effects accompanying vaporization and other allotropic changes in materials are measured by heats of vaporization and heats of transformation.

When a chemical compound is formed from its elements, heat is either liberated or absorbed. The heat of formation, designated by ΔH_f, of a substance is the enthalpy change resulting from a reaction in which the reactants are initially in the elemental form at some specified temperature and pressure, and the product is obtained at the same conditions of temperature and pressure. The heat of formation is a special case of heat of reaction in which the reactants are pure elements. The usual conditions of temperature and pressure are at the base temperature 25°C and 1 atmosphere, in general, and the heat of formation under these conditions is termed the standard heat of formation. A compound whose heat of formation is negative is termed an exothermic compound while one whose heat formation is positive is termed an endothermic compound.

The heats of reaction may be computed from the heats of formation by the following equation:

$$\Delta H = \Sigma[\Delta H_f \text{ of reaction products}] - \Sigma[\Delta H_f \text{ of reactants}] \qquad \text{II-12}$$

The above equation follows from the previously indicated fact that ΔH for any process depends only on the initial and final states and not on the path taken. Thus, if a process is divided into several steps and ΔH is determined for each step, the algebraic sum of the ΔH values for all the steps must equal ΔH for the original direct process.

The enthalpies involved in the formation of solutions are functions of composition. The enthalpy changes accompanying the formation of solutions have been tabulated for a few systems. Fortunately, these heats of solution in many cases are small compared with other enthalpy changes in the process, so that they can often be neglected without introducing serious errors into the over-all heat balance.

The heat balance for a process is a statement of the energy balance in a form which is convenient. The heat balance, like the material balance, accounts for heat quantities in two categories, input and output. The totals for the two categories must be equal. All items in the heat balance are positive, so if simple rules are followed there is little confusion of negative and positive signs which is often experienced in thermodynamic calculations.

No new principles are introduced in the heat balance; it involves the same principles utilized in the mass balance. However, a few conventions and definitions are involved in order to insure proper classification of the energy input and output.

It is necessary to select a single base or reference temperature. This base temperature is often 25°C. However, for high temperature processes one might select the temperature of the process as the base temperature. Thus steel-making processes might be referred to 1600°C, or copper-converting processes to 1200°C. After selecting the reference temperature, reference states at this temperature must be understood for each substance in the input and output streams. For most substances there is only one stable state at the reference temperature. However, in many cases, particularly for solutions, a specification is necessary.

The sensible heat of an input or output material is the positive quantity of heat required to change the substance from the reference temperature and reference state to the actual temperature and actual state in which it is present in the input or output of the process. Thus, if the reference temperature is 1600°C, and the material enters the process at that temperature and in its reference state, the substance brings no sensible heat into the process. On the other hand, if the substance is brought into the process at ambient air temperatures, it brings a negative sensible heat into the process. The calculation of sensible heat is a calculation of ΔH for the heating from the reference state to the actual state.

Heats of reaction must have the values corresponding to the reference temperature, and not to the process or to other temperatures, and must be for the reactions between substances in their reference state at the base temperature.

The heat balance thus includes:

Input 1. Sensible heats in input materials (positive)
2. Heats evolved in exothermic reactions
3. Heats supplied from outside the system.

Output 1. Sensible heats in output materials
2. Heats absorbed in endothermic reactions
3. Heats absorbed in bringing input materials to reference temperature and state
4. Heat loss to surroundings by radiation and convection.

The procedure in calculating a heat balance is essentially the same as that involved in calculating a material balance. Accordingly, a logical and standard procedure of calculation is desirable, and should be outlined prior to the solution of the problem.

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CHAPTER III

THERMODYNAMICS

The chemical behavior of materials and the influence of extensive properties on the reactions which take place between substances may be described in terms of thermodynamic relationships.

The total energy which is available from a chemical reaction to do reversible work is the free energy, a quantity which was defined by J. Willard Gibbs as:

$$F = H - T S \qquad \text{III-1}$$

Then for a chemical reaction at constant temperature:

$$\Delta F = \Delta H - T \Delta S \qquad \text{III-2}$$

The free energy change, ΔF, is a measure of the driving force for the occurance of the reaction at a definite pressure and temperature. When ΔF is negative the reaction tends to occur and conversely, when ΔF is positive the reverse reaction tends to occur. The greater the free energy change, the greater the tendency for the reaction to occur. When ΔF is zero, the reaction is said to be in equilibrium and there is no tendency for the reaction to occur in either direction. The free energy change does not determine the rate of the reaction and will not permit a prediction as to whether the reaction is fast or slow.

Solutions

The chemical activity, $\underline{a}$, (the tendency of a component of a phase to react), is dependent upon concentration of the component in that phase. In an ideal solution, the chemical activity of a component is proportional to the amount of the component present. As an example, if liquid nickel and iron are mixed in equal mole fractions, the iron which is present would have one half the chemical activity of pure liquid iron. If the solution were more dilute in iron, its activity would be less. A component whose activity is proportional to mole fraction is said to be ideal and to obey Raoult's Law:

$$a_A = \frac{\text{moles A}}{\text{Total moles}} = \frac{N_A}{N} \qquad \text{III-3}$$

At $N_A = N$ in Equation (III-3), $a = 1$. Thus, the pure phase is the reference concentration or the Standard State. The reference concentration could also have been chosen at some other point. For example, a 1 mole percent solution could be used as the standard state and the activities indexed from that point. Then, an ideal solution would have component activities equal to mole percent, i.e., a 1 mole percent solution would have an activity equal to 1, whereas a pure solution of a component would have an activity (index) of 100.

Other standard states are often used as well. For a gas, the standard state is usually taken as 1 atmosphere pressure of that particular gas component. An ideal gas with a partial pressure of 1 millimeter of mercury would have an activity of 1/760. If however, 1 millimeter of mercury pressure had been chosen as the standard state, the activity would be equal to 1 if the gas component was at a pressure of 1 millimeter and equal to 760 at one standard atmosphere. In metallic solutions, a standard state is often chosen such that the activity is equal to the concentration in weight percent at infinite dilution. This standard state, referred to as the one weight percent solution, is often convenient since compositions are generally expressed in weight percent.

Free Energy and Activity

The free energy of a component is related to the chemical activity of the component by the relationship:

$$\bar{F} - \bar{F}^{o} = 4.575\ T \log_{10}(a) \qquad \text{III-4}$$

where $\bar{F}$ is the free energy of the component within the phase and $\bar{F}^{o}$ is the free energy of the component in its standard state in which $a^{o} = 1$.

Non-Ideal Solutions

Most real solutions are not ideal. In order that a solution be ideal, the atomic species of the component must interact with those of the other components in the same manner that they do with their own. If this is not the case, the chemical activity of the component is altered from ideal behavior.

The activities of nickel and silicon in molten iron are shown in Figures III-1 and III-2. Nickel, as previously discussed, behaves ideally but silicon does not. The silicon atoms are more strongly associated with the iron atoms than with other silicon atoms, thus lowering the chemical activity of silicon below the ideal behavior prediction. The strong association between silicon and iron atoms is indicated by the facts that (1) energy is given off (exothermic heat of solution) when silicon is added to iron, and (2) intermetallic compounds of iron and silicon are readily formed in the solid phase.

Figure III-3 shows the activity of copper in iron. Unlike silicon, copper atoms do not associate as readily with iron atoms as with other copper atoms. Therefore, the chemical activity of copper is increased above that predicted on the basis of ideal behavior. This is also shown by (1) endothermic heat of solution of copper, and (2) the

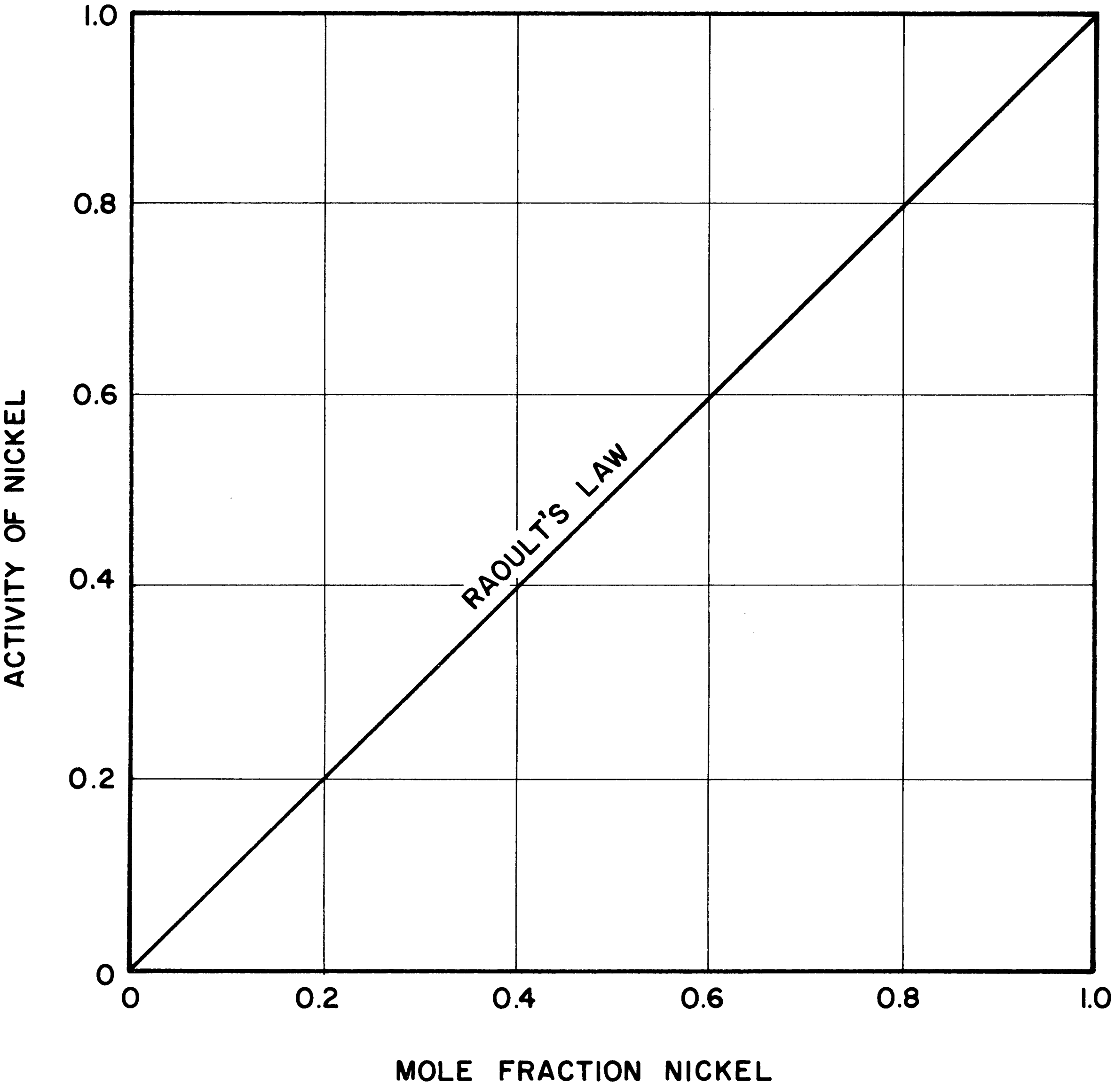


Figure III-1. Activity of Nickel in Liquid Iron Showing Ideal Behavior.
(Standard State: Pure Liquid Nickel)

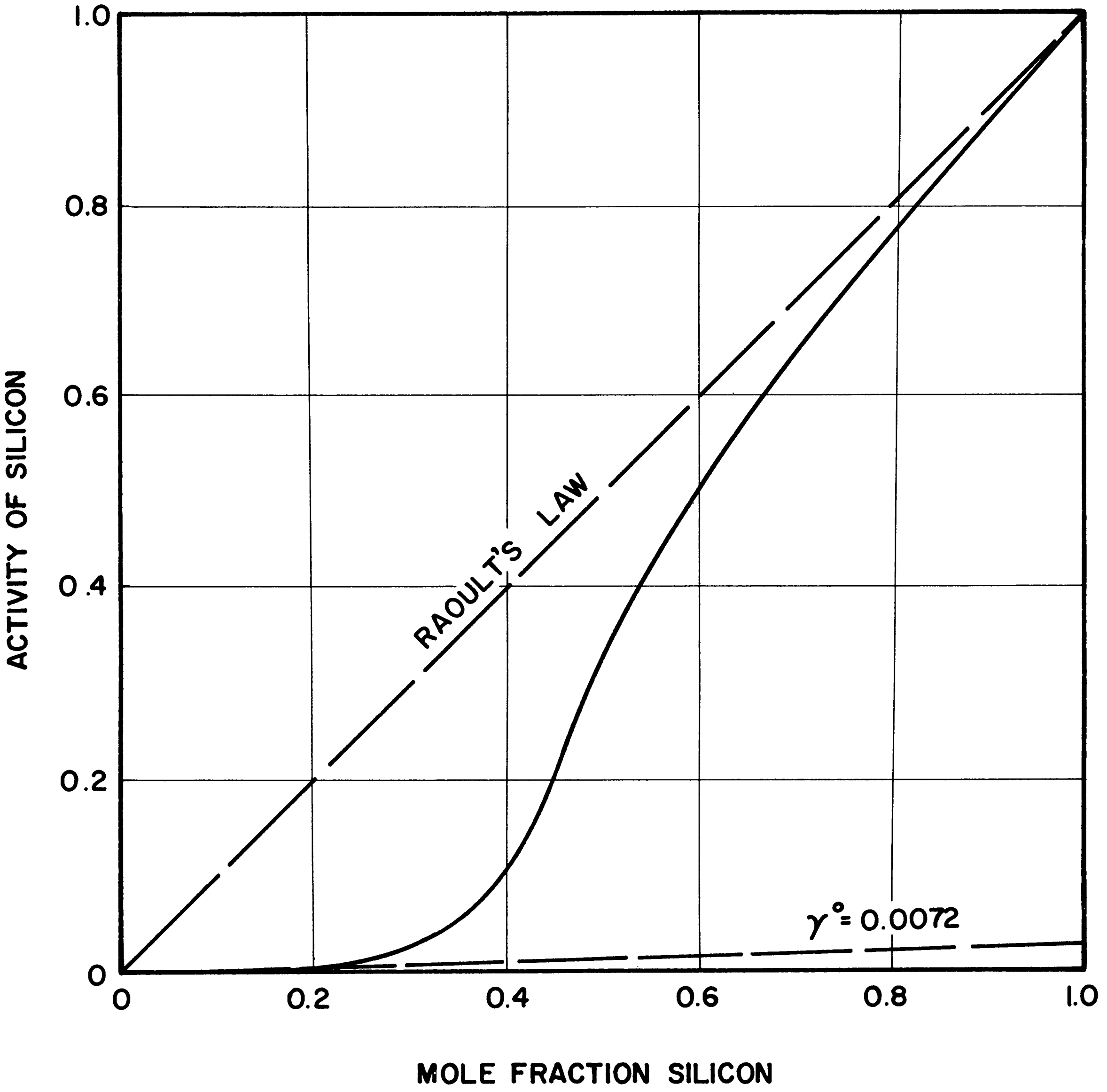


Figure III-2. Activity of Silicon in Liquid Iron at 1600°C. (Standard State: Pure Liquid Silicon)

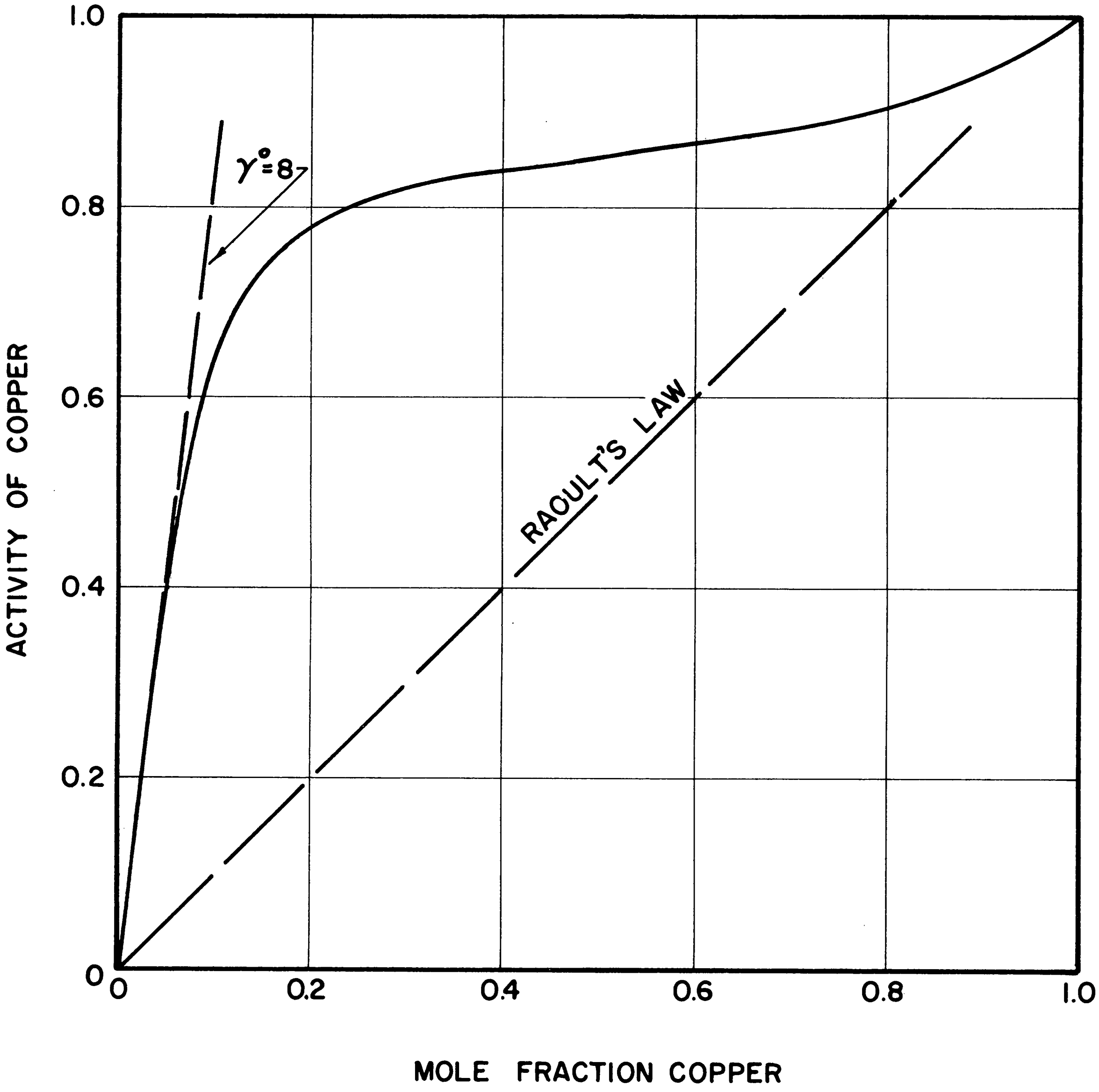


Figure III-3. Activity of Copper in Liquid Iron at 1600°C. (Standard State: Pure Liquid Copper) tendency to form two immiscible liquids at temperatures near the liquidus.

Although copper and silicon do not behave ideally, it is observed that their activities are proportional to concentration in dilute solutions. This quasi-ideal behavior is described by Henry's Law which says that the activity is proportional to concentration in dilute solutions. For this case it is convenient to use the 1 weight percent solution as a reference state. Figures III-4 and III-5 show Henry's law behavior for copper and silicon in molten iron.

Few solutions are ideal, or even quasi-ideal, and it is necessary to take this into account when calculating activities from concentrations. This is done by means of an activity coefficient. Figure III-6 shows the activity coefficient necessary to calculate the activity of carbon in iron on the basis of Henry's Law. The activity coefficient is defined as:

$$a = f * (\text{wt.}\%) \qquad \text{III-5}$$

The activity coefficient of carbon is 1 in very dilute solutions, i.e. carbon obeys Henry's Law. As the concentration is increased, the activity coefficient exceeds 1 by increasing amounts.

For deviations from Raoult's Law, Equation (III-5) may be expressed as:

$$a = \gamma * (\text{mole fraction}) \qquad \text{III-6}$$

Conversion from One Standard State to Another

It is frequently necessary to convert from one standard state to another in order to make use of data which may give ΔF^o as a function of temperature relative to a reference state which differs from the desired one. For example, the free energy of formation of a metal oxide may be known for the reaction:

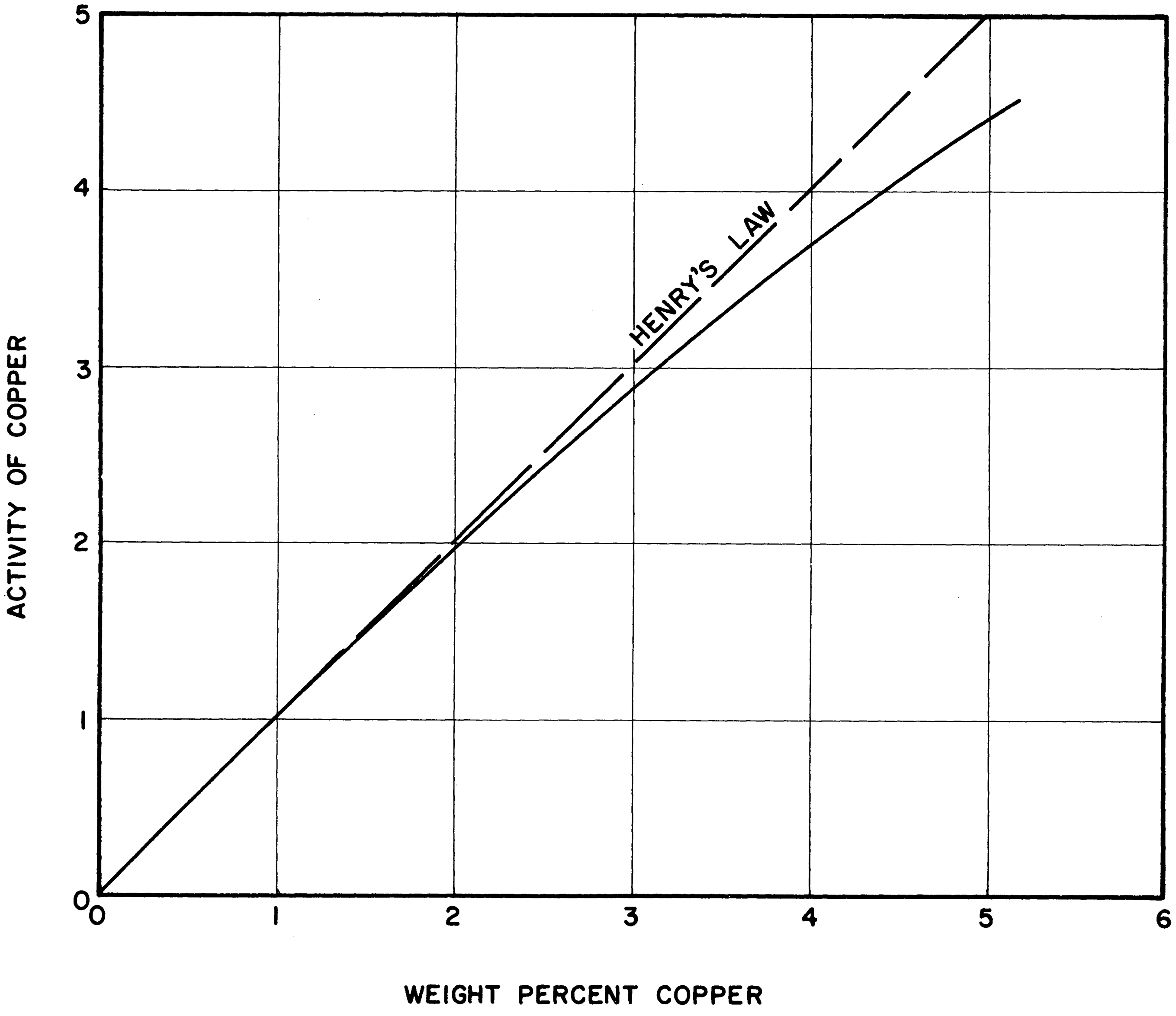


Figure III-4. Activity of Copper in Liquid Iron at 1600°C. (Standard State: Infinite Dilution Referred to One Weight Percent Solution)

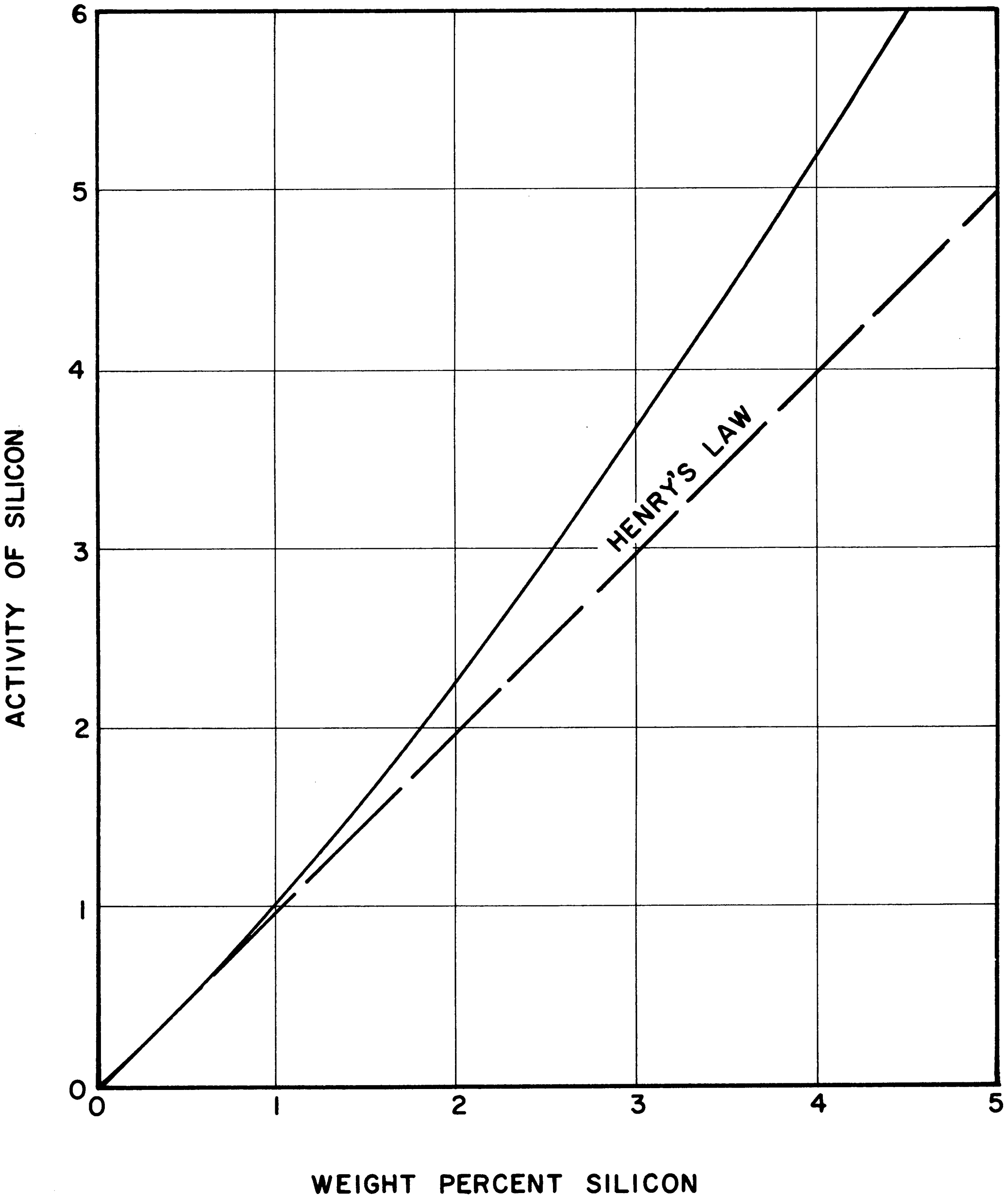
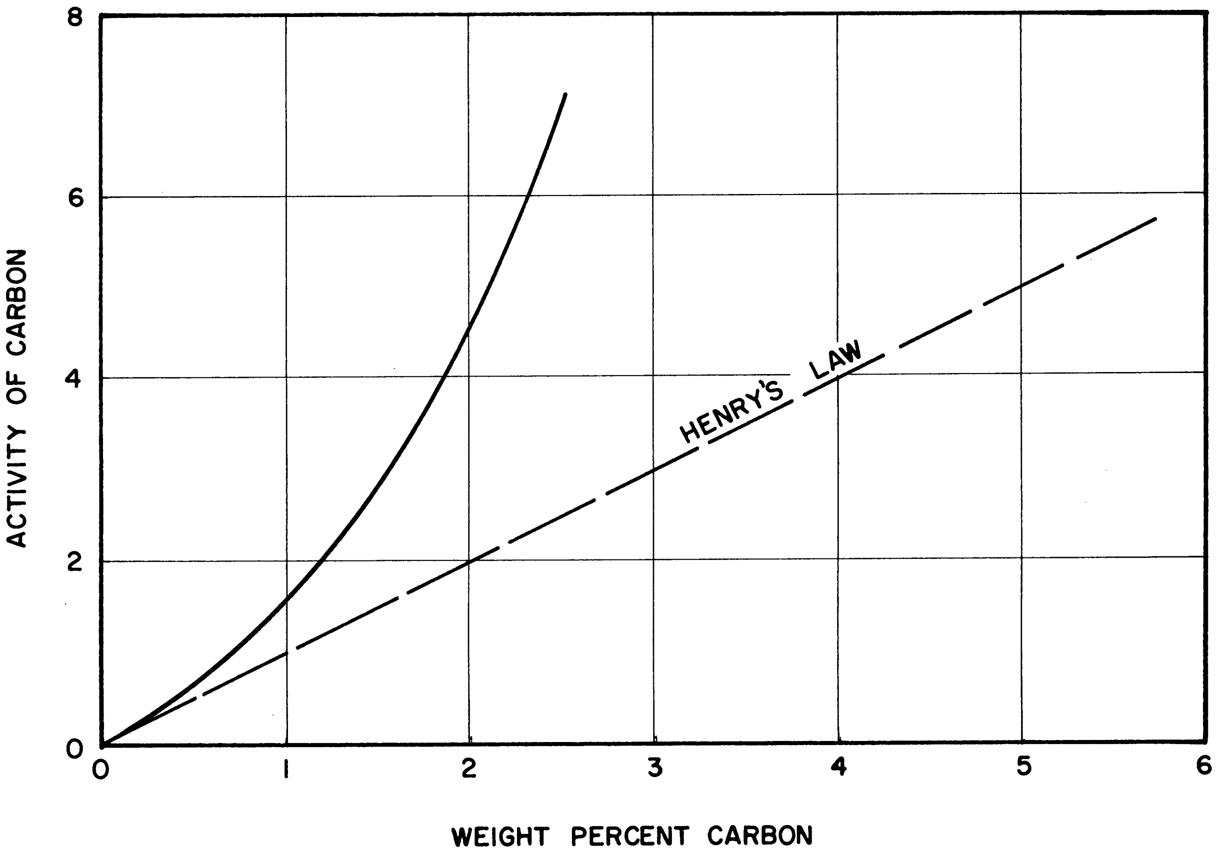


Figure III-5. Activity of Silicon in Liquid Iron at 1600°C. (Standard State: Infinite Dilution Referred to One Weight Percent Solution)



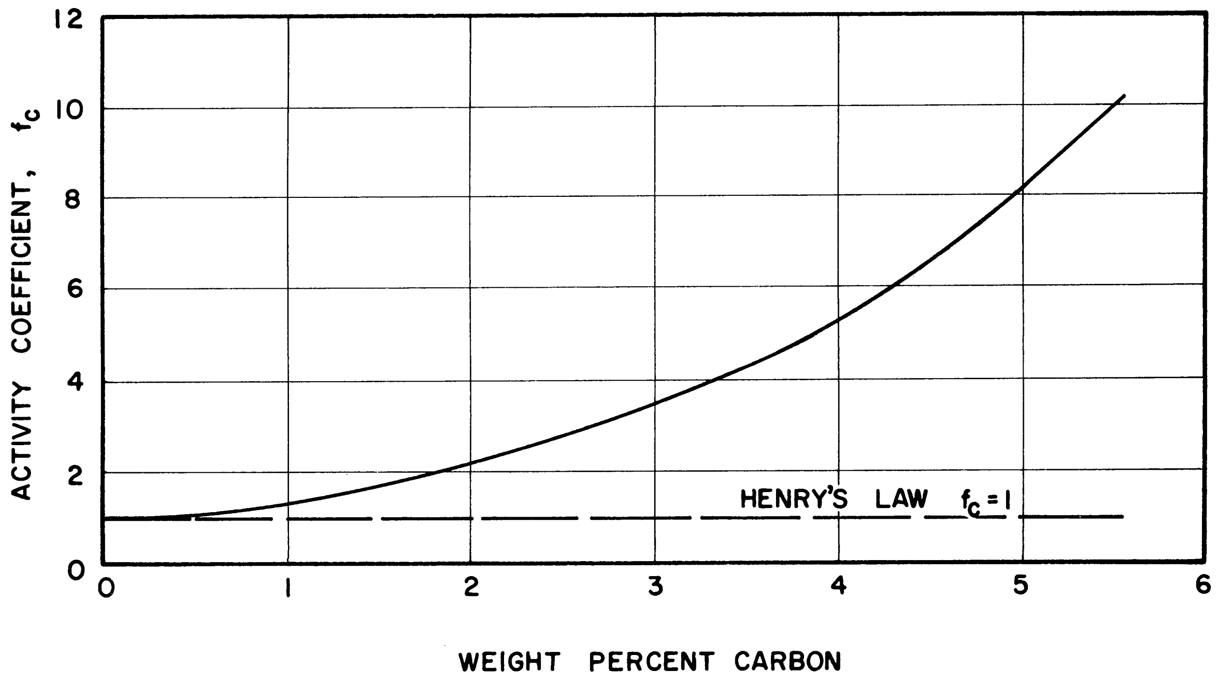


Figure III-6. Activity and Activity Coefficient of Carbon in Liquid Iron at 1600°C.
(Standard State: Infinite Dilution Referred to One Weight Percent Solution)

$$M(\text{pure liquid}) + O_2(\text{gas}) = MO_2(\text{solid}) \qquad \text{III-7}$$

but the oxidation of interest occurs from solution in a liquid metal solvent, say liquid iron. The activity of the metal must then be expressed in terms of its concentration in solution in liquid iron.

Figure III-7 shows the activity of the metal, M, in solution in iron as a function of mole fraction, N_M. It is seen that the free energy change involved in the transfer of M from the pure liquid State A, to the dilute solution in iron, State B, must be determined. The free energy change is given by the expression:

$$\Delta F = R\ T\ \ln\ (a_{M(\text{solution})}/a_{M(\text{pure liquid})}) \qquad \text{III-8}$$

The activity ratio for the two Standard States is given by the atom fraction ratio, provided that the atom fraction in the solution is modified by the activity coefficient, γ^{o}, as shown in Figure III-7. The atom fraction of component M in solution in iron is given by the expression:

$$N_M = \frac{\frac{c}{M}}{\frac{c}{M} + \frac{100-c}{55.85}} \qquad \text{III-9}$$

where c is the weight percent and M is the atomic weight of component M. Equation (III-9), when applied to a dilute solution, reduces to:

$$N_M = c\ \frac{0.5585}{M} \qquad \text{III-10}$$

If the standard state in solution, State B in Figure III-7, is chosen such that the activity relative to that standard state is equal to the concentration in weight percent, c may be set equal to 1, (the reference state of a one weight percent solution, i.e., a = 1 at one weight percent). Correcting the mole fraction in solution for deviation from Raoult's Law, and noting that the activity in the pure liquid, State A

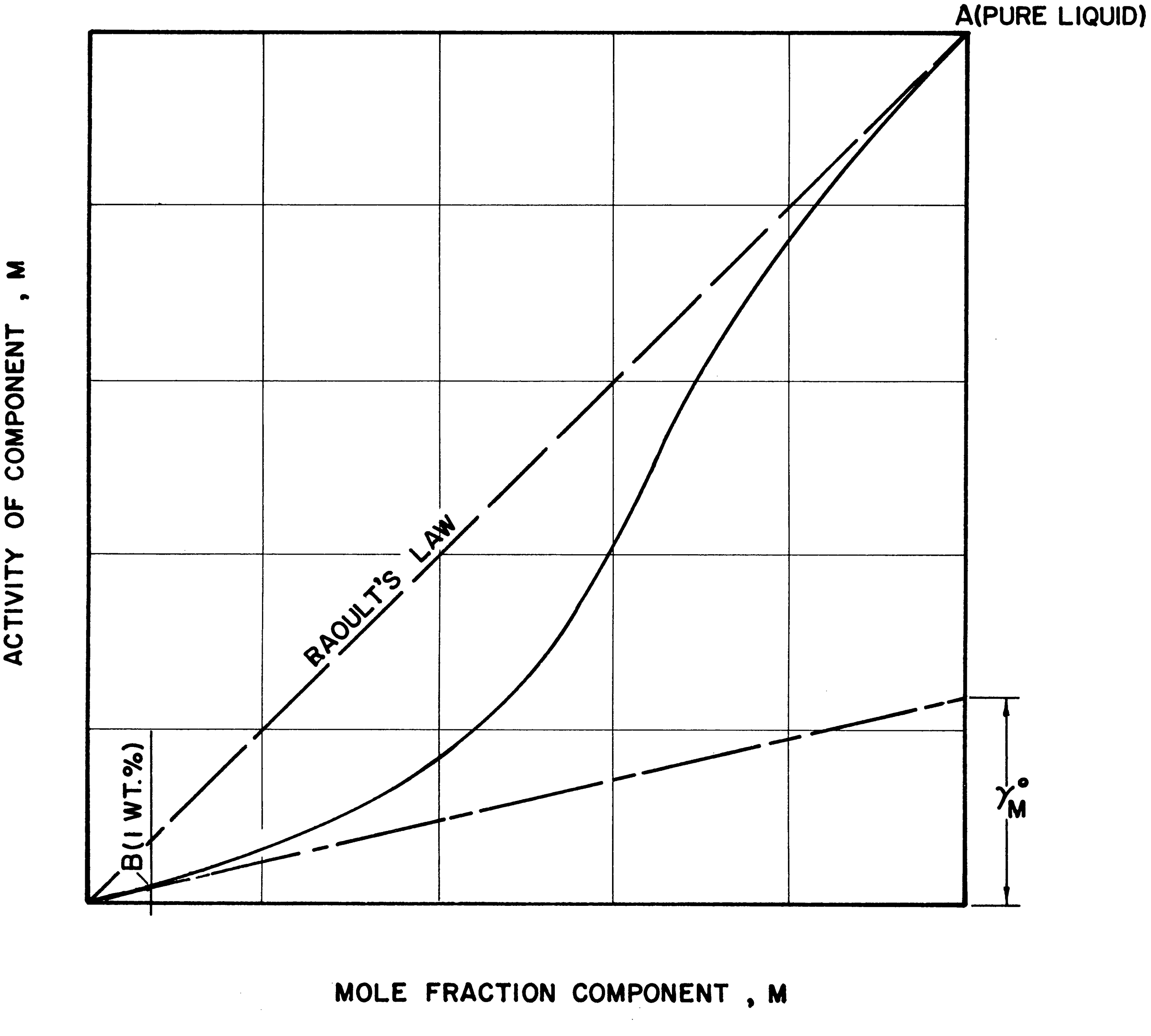


Figure III-7. Activity-Composition Diagram Showing Factors Involved in Converting Activities from One Standard State to Another.

in Figure III-7, is unity, the free energy change corresponding to the conversion of standard states from the pure liquid to infinite dilution referred to a one weight percent solution is given as:

$$\Delta F = R\ T\ \ln\ (0.5585\ \gamma^{\circ}/M) \qquad \text{III-11}$$

Equation (III-11) is the free energy change for the reaction:

$$M\ (\text{pure liquid}) = M\ (1\ \text{wt.}\ \%\ \text{solution}) \qquad \text{III-12}$$

Subtracting Equations (III-7) and (III-12),

$$M(1\ \text{wt.}\ \%\ \text{solution}) + O_2(\text{gas}) = MO_2(\text{solid}) \qquad \text{III-13}$$

for which the standard free energy change is:

$$\Delta F^{\circ} = \Delta F^{\circ}_{\text{III-7}} - 4.575\ T\ \log\ (0.5585\ \gamma^{\circ}/M) \qquad \text{III-14}$$

The equilibrium constant for Equation (III-13) involves the concentration of M in iron in weight percent.

The development above is equally valid for other solutions and with suitable modifications may be adopted for other equilibria and for solvents other than iron.

Effect of Temperature on Equilibrium Constant

The free energy change for a reaction was defined by Equation (III-2) which may be written for a reaction in which the reactants and products are in their standard states as:

$$\Delta F^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \qquad \text{III-15}$$

Expressing Equation (III-15) in terms of the equilibrium constant:

$$\log K = -(\Delta H^{\circ}/4.575\ T) + (\Delta S^{\circ}/4.575) \qquad \text{III-16}$$

At the high temperatures involved in most metallurgical processing operations, ΔH° and ΔS° vary only slightly with temperature, so slightly that experimental techniques are seldom sensitive enough to determine them. Consequently, the enthalpy and entropy changes may be assumed to be independent of temperature over reasonably small temperature ranges.

Effect of Pressure on Equilibrium Constant

Le Chatelier's principle states: "any change of the factors controlling the equilibrium of a system produces a shift in such a direction as to minimize the change of the factor concerned". In terms of temperature this means that:

1. endothermic reactions are more complete at higher temperatures, and
2. exothermic reactions are favored by lower temperatures.

A second aspect of this principle is encountered in regard to pressure changes. They are:

1. higher pressures shift the equilibrium toward smaller volumes, and
2. reactions with volume increases are favored by lower pressures.

This generalization is most important for those reactions which have unequal numbers of moles of gas in their reactants and products.

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CHAPTER IV

KINETICS

Chemical kinetics is a study of the rate at which chemical reactions occur. Reaction rates are important in the design of processes because they determine the size of equipment and the time involved in processing material with it, and therefore have much to do with economic feasibility. There are two general scientific approaches to the problem of describing a metallurgical process. The first approach as outlined in Chapter III was the thermodynamic approach. The thermodynamic method permits the process to be described in terms of an end point to which the process will eventually converge or one which it is approaching during its operation. The second approach which will be now considered is that of reaction kinetics. This implies a knowledge of the mechanisms by which chemical reactions occurring in the process take place and a mathematical description of the process reactions in terms of those mechanisms.

The foundation of present rate theory goes back historically to Arrhenius, who found that for many processes the specific reaction rate constant k may be written as a function of temperature in the following way:

$$k = Ae^{-Q/RT} \qquad \text{IV-1}$$

Alternatively, log k is a linear function of 1/T. The quantity Q although usually determined only from the slope of such a plot is regarded as the heat or energy of activation of the reaction. This relationship is parallel to the one corresponding to the equilibrium constant.

The Theory of Absolute Reaction Rates

Many have contributed to the development of the theory of absolute reaction rates. An outstanding number of successful applications have been made Eyring and co-workers.[1]

Modern rate theory assumes that any observable process may be described adequately in terms of the energy of the atomic configurations involved. For any conceivable way the reaction might occur we may imagine a plot of energy versus a distance coordinate as shown in Figure IV-1. The curve of the reaction coordinate involves a peak or a maximum through which the reaction must pass, corresponding to what is termed the activated complex. The two fundamental principles involved in the reaction rate theory are both concerned with the activated complex. They are:

1. The activated complex has an exceedingly short life and is in equilibrium with the reactants. A chemical equation for the formation of the activated complex may be written and an equilibrium constant determined. This equilibrium constant is related to the free energy of formation of the activated complex in the standard state in the usual way.

$$\Delta F^* = -RT \ln K^* \tag{IV-2}$$

2. The specific rate of decomposition of the activated complex into products is a universal rate independent of the nature of the particular reaction or complex involved. The rate is RT/Nh, where R is the gas constant, h is Planck's constant and N is Avogadro's number.

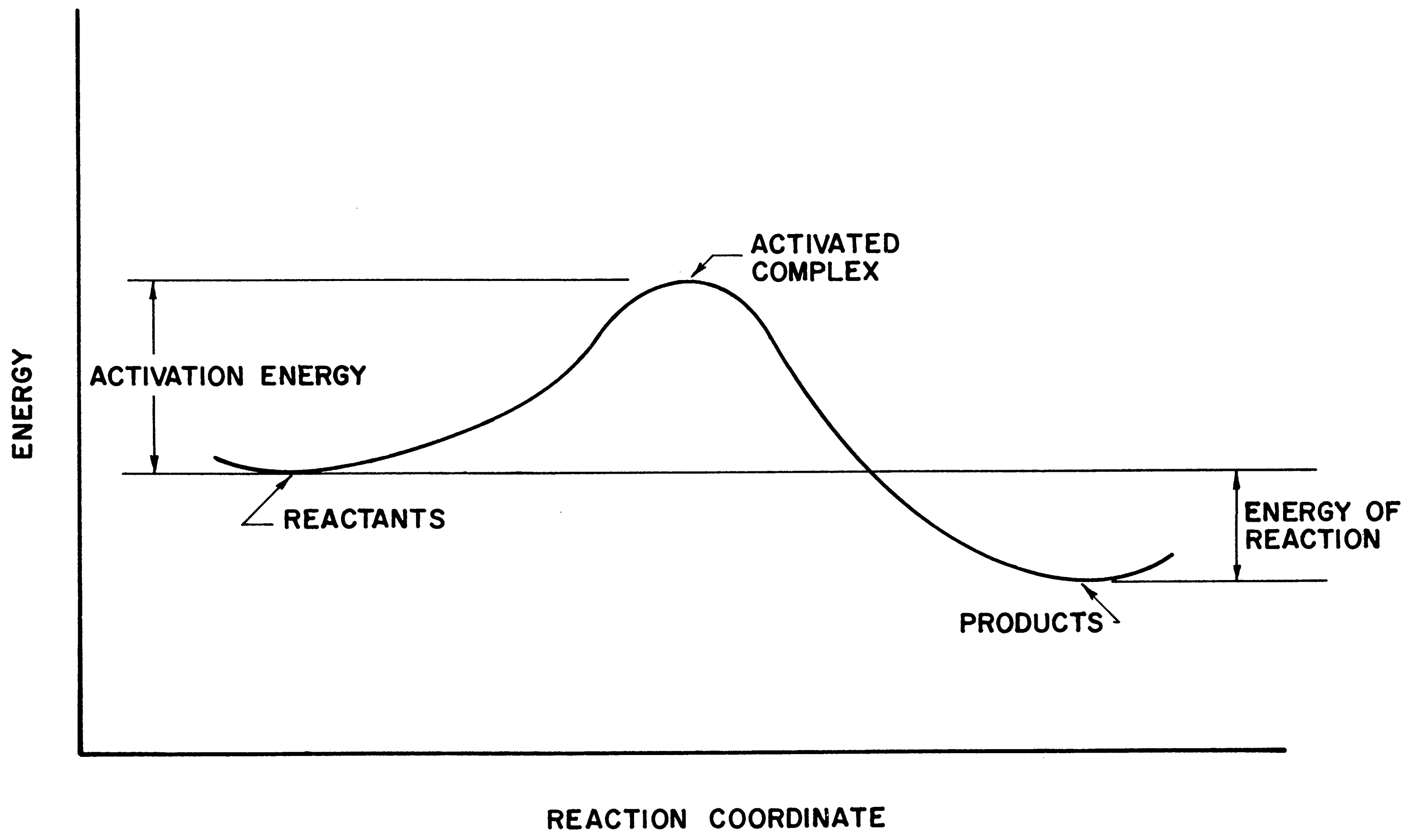

Figure IV-1. Potential Energy Path for a Chemical Reaction.

The reaction rate may then be expressed as:

$$\begin{aligned} \text{reaction rate} = [RT/Nh]\ e^{-\Delta H^*/RT}\ e^{\Delta S^*/R}\ & [\gamma_{R_1} \gamma_{R_2} \cdots\cdots \gamma^*] \\ & [c_{R_1}\ c_{R_2}\ \cdots\cdots] \end{aligned} \qquad \text{IV-3}$$

The following facts are to be noted about the terms of the above reactions:

1. The first term contains only universal constants and the absolute temperature.
2. The second term is the principal temperature dependent term involving the enthalpy of activation.
3. The third term depends upon the entropy of formation and it is expected if the complex is simple that ΔS^* is quite small, but that if the complex is complicated (as compared with the reactant) in atomic configuration ΔS^* is large and negative.
4. The fourth term involves the activity coefficients.
5. The fifth term is the product of the concentrations of the reactants.

A complete description of the absolute reaction rate theory may be found in the literature and an excellent simplified treatment has been presented by Darken.[2]

Classification of Reactions

A reaction may be classified according to its molecularity, that is, the number of molecules or molecules plus atoms taking part as reactants in the formation of the activated complex. On this basis the elementary steps of any over-all reaction are designated monomolecular, bimolecular, trimolecular and so forth. An over-all reaction involving many steps, however, cannot properly be classified in this manner, that is, only the individual elementary steps of an over-all reaction are suitably described in this way.

Over-all reactions are commonly classified empirically according to the number of concentrations to which the rate is proportional. The reaction order may be defined as the sum of the powers to which the concentrations of the reactants must be raised to give a satisfactory solution to the rate equation.

In many simple cases, the observed over-all reaction proceeds principally by one chain or sequence of steps and one step is so much slower than the others that it alone is essentially responsible for the observed rate. This slow step involves, as do all steps, the formation of an activated complex and its decomposition. If this step is unimolecular, the rate of the over-all reaction will be of the first order. The reaction rate is the rate of disappearance of reacting species which is then proportional at constant temperature to the concentration:

$$-dC/dt = kC \qquad \text{IV-4}$$

Upon integration, this gives

$$\ln C_o/C = k\ (t - t_o)$$

where C_o is the initial concentration at time t_o. For kinetic treatments of more complicated cases, the reader is referred to the sources given at the end of the chapter.

Mass Transport as Rate-Limiting Step

At the high temperatures which are usually involved in metallurgical processes the rates of chemical reactions are in general very large. Consequently, the rate-determining step is most often that of mass transport. For the formal development of the fundamental diffusion equations, the reader is referred to the references at the end of the chapter. It should be noted that an excellent presentation of these equations and suitable boundary conditions for them are presented by Darken[2].

Transport in solids is by diffusion and is therefore governed by Fick's laws. If the rate of a reaction is limited by diffusion in a solid phase, the rate may be expected to be low.

In fluids (gases and liquids) transport occurs by diffusion and convection. Generally forced convection is encountered and under these conditions the composition of the bulk of the fluid is practically uniform, with appreciable concentration differences only close to the phase boundary. This is represented schematically in Figure IV-2 for a case where a reaction product denoted as i is being removed by the fluid. The rate of transport of i away from the boundary is in moles per second-centimeters squared:

$$\frac{\mathring{n}_i}{A} = -D_i \left(\frac{\partial C_i}{\partial x}\right) + C_i v_x \qquad \text{IV-5}$$

where D_i is the diffusion coefficient, A the phase boundary area, c_i the concentration of i and v_x is the flow velocity of the liquid in the x direction, $c_i v_x$ represents the convection contribution to the transport; v_x cannot normally be evaluated, but at the boundary $v_x = 0$. Hence,

$$\frac{dn_i}{dt} = -Di \cdot A \left(\frac{\partial C_i}{\partial x}\right)_{x=0} \qquad \text{IV-6}$$

as Figure IV-2 shows:

$$\delta_i = \frac{Ci\ (\text{bulk}) - Ci\ (x=0)}{(\partial Ci/\partial x)_{x=0}} \qquad \text{IV-7}$$

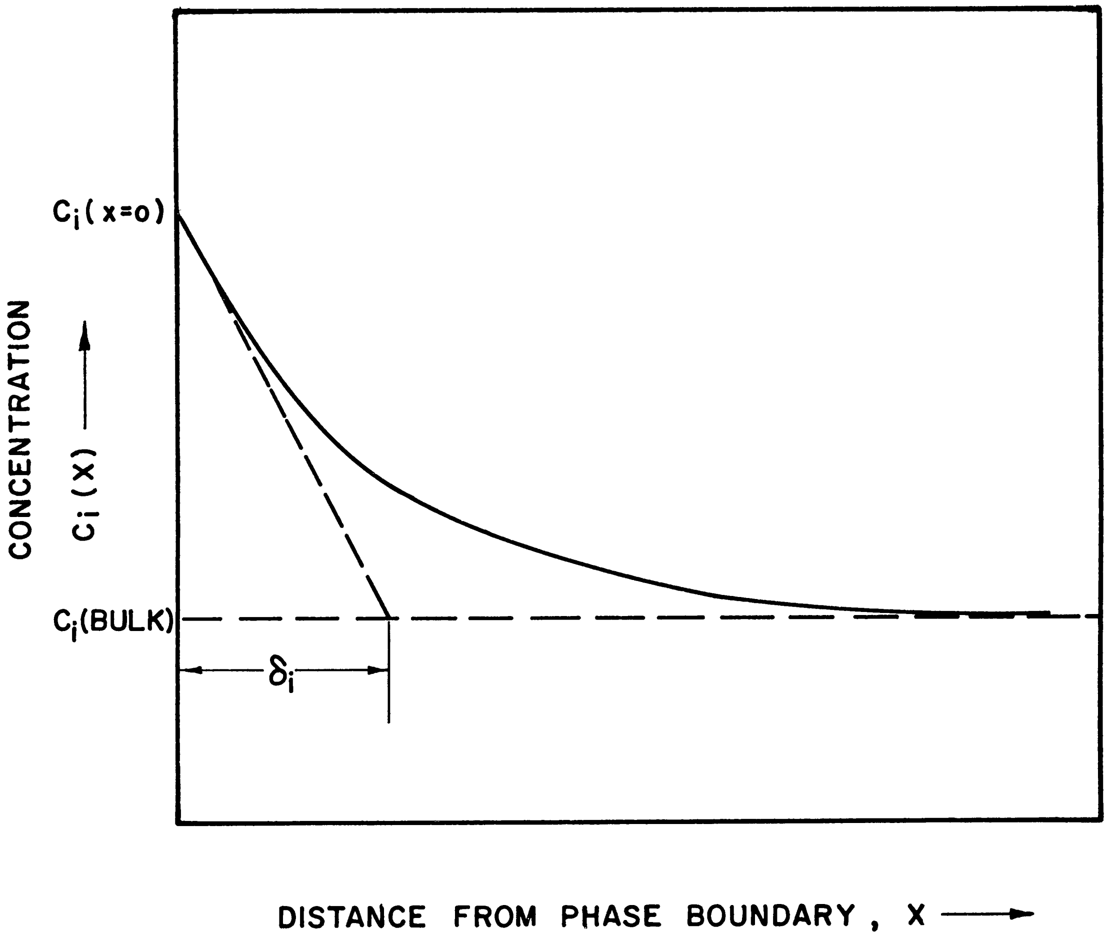

Figure IV-2. Concentration Profile in a Boundary Layer.

so:

$$\frac{dn_i}{dt} = \frac{D_i}{\delta_i} A\ [C_i\ (x=o) - C_i\ (\text{bulk})] \qquad \text{IV-8}$$

where δ_i is the effective boundary layer thickness. In general, δ cannot be calculated except for a few cases, but its value depends upon D, being larger for larger values of D, and also on the convection conditions, being smaller for higher flow velocities past the boundary. When the reaction is between a gas mixture and a liquid solution or between two liquids, one must consider two boundary layers, one in each phase.

Darken[2] has applied the above general development to the carbon boil in the open hearth process, by assuming that the situation prevailing in the open hearth is essentially that of oxygen diffusion from a slag through a thin layer or film in the metal phase (neglecting the boundary layer in the slag phase) and mixing by convection beyond this film. Darken has calculated the rate of carbon drop estimating the film thickness to be about 0.003 centimeters and choosing a reasonable value for the diffusivity.

From Fick's first law, it may be shown that the rate of carbon drop on the basis of this model is:

$$-d[C]/dt = D\ \frac{([O]_{se} - [O])}{l \times \delta}\ \frac{12}{16} \qquad \text{IV-9}$$

where l is the bath depth and δ the film thickness. For conditions during oreing, the following average or approximate values may be used; $[O]_{se} = 0.23\%$ (solubility limit at 1600°C), $[O] = 0.04\%$, $l = 13.5$ inches = 34 centimeters (average bath depth), $D = 1 \times 10^{-4}$ centimeters^2/second, and $\delta = 0.003$ centimeters.

On this basis,

$$\frac{-d[C]}{dt} = 1 \times 10^{-4}\left(\frac{0.23-0.04}{34\times0.003}\right)\frac{12}{16} \times 3600 = 0.50\%/\text{hr} \qquad \text{IV-10}$$

which is in good agreement with the observed carbon drop during heavy oreing. A similar calculation for the rate of carbon drop during normal boil conditions setting $[O]_{se} - [O] = 0.04$ gives 0.11% per hour, a figure very close to the observed average rate.

It should be noted from the above example that selection of suitable rate data permit the process designer to predict the kinetic behavior of a process. T. B. King[6] has presented a number of excellent examples which are applicable to metallurgical processes operating under vacuum conditions.

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CHAPTER V

THE THERMOCHEMICAL MODEL

A thermochemical model of a process is a dynamic description of the process taking into account mass and heat transfer, and kinetics, along with instrumentation and control. The model permits an accurate method of calculating the operating characteristics of a process under all possible conditions, including variations in process temperatures, pressures, flow rates, and feed compositions. The complete model is suitable for adaptation as a computer program program permitting simulation of the process and dynamic predictions of its operating characteristics or optimization of the process under a given set of limiting conditions. This will be treated in greater detail in Chapter XXVII.

It should be noted that the thermochemical model, or often only a limited form of it, is the first step toward good process design. In order to merely specify the size of a process, a general knowledge of the desired input and yield are necessary. This can be given by a mass balance of the system, often based on the experience with previous equipment of a similar type. In addition, the energy or fuel requirements are equally important. The completion of a mass and energy balance for a process is often sufficient to quantitatively evaluate the effect of changes in process operating variables on the performance of the process.

Mass Balance

The mass balance is the most important part of the thermochemical model. The mass balance may be written on the basis of previous experience or on the basis of known equilibrium relationships. The principles of writing a mass balance were outlined in Chapter II. The purpose of this section is to introduce some of the difficulties which may be experienced in practice, and indicate some of the approximations which are often advantageous to make in order to achieve the goal of a reasonably accurate set of material relationships.

In practice, overlapping data are often available which permit a check on the mass balance. Data on an iron blast furnace, for example, might give the mass of the inlet and outlet streams as well as their composition. It is possible, however, that the balance for a given element may not check!! Once one has ruled out the possibility of accumulation or depletion of the element from somewhere inside the system (a real possibility under conditions where the burden is altered or new refractories are used to reline the process container), a decision must be made regarding the relative accuracy of the data, and on which part of the data the balance should be based. In making this decision, the methods used to determine the data must be given consideration.

Furthermore, the alternative difficulty of having insufficient data may occur. In this case, previous experience and the astute judgement of the process engineer are brought to bear on the problem. Lacking hot metal analyses, in the case of the blast furnace cited above, for elements which are strong oxide formers, one can safely assume that these elements report completely in the slag. Such elements would include calcium, magnesium, and aluminum, but would not include silicon!! The assumption that all elements which are not strong oxide formers report in the hot metal is also a reasonably valid one. Such elements would include iron and manganese.

In the face of missing thermodynamic and kinetic data, the assumption that a given reaction goes to completion within the alloted process time is often a valid basis for design purposes. Consider for example, the Dortmund-Hörder degassing process in which low carbon steel is drawn by vacuum from a ladle up into a vacuum chamber, and then released to flow by gravity back into the ladle. A schematic description of the process is shown in Figure V-1. Only a small fraction of the liquid metal in the ladle can be drawn up into the vacuum chamber. The question facing the process designer is: "How many cycles of the degassing operation will be required to lower the gas content of the metal in the ladle to a desired level?".

An approach to the problem which would appear feasible is to assume that the metal drawn up into the vacuum chamber is completely degassed, and that upon being returned to the ladle is completely mixed with the ladle material. For this case, the material balance for the degassing operation is given by the relation:

$$C = C_o (1 - X)^n \qquad \text{V-1}$$

where: n = number of cycles

C = concentration of gas in the metal in the ladle after the nth cycle.

C_o = initial gas concentration in the metal

X = fraction of ladle material which is drawn into the vacuum chamber during each cycle.

The results of actual data taken from the operation of the process are compared with Equation (V-1) in Figure V-2. The agreement between the two curves shows the assumption to be valid.

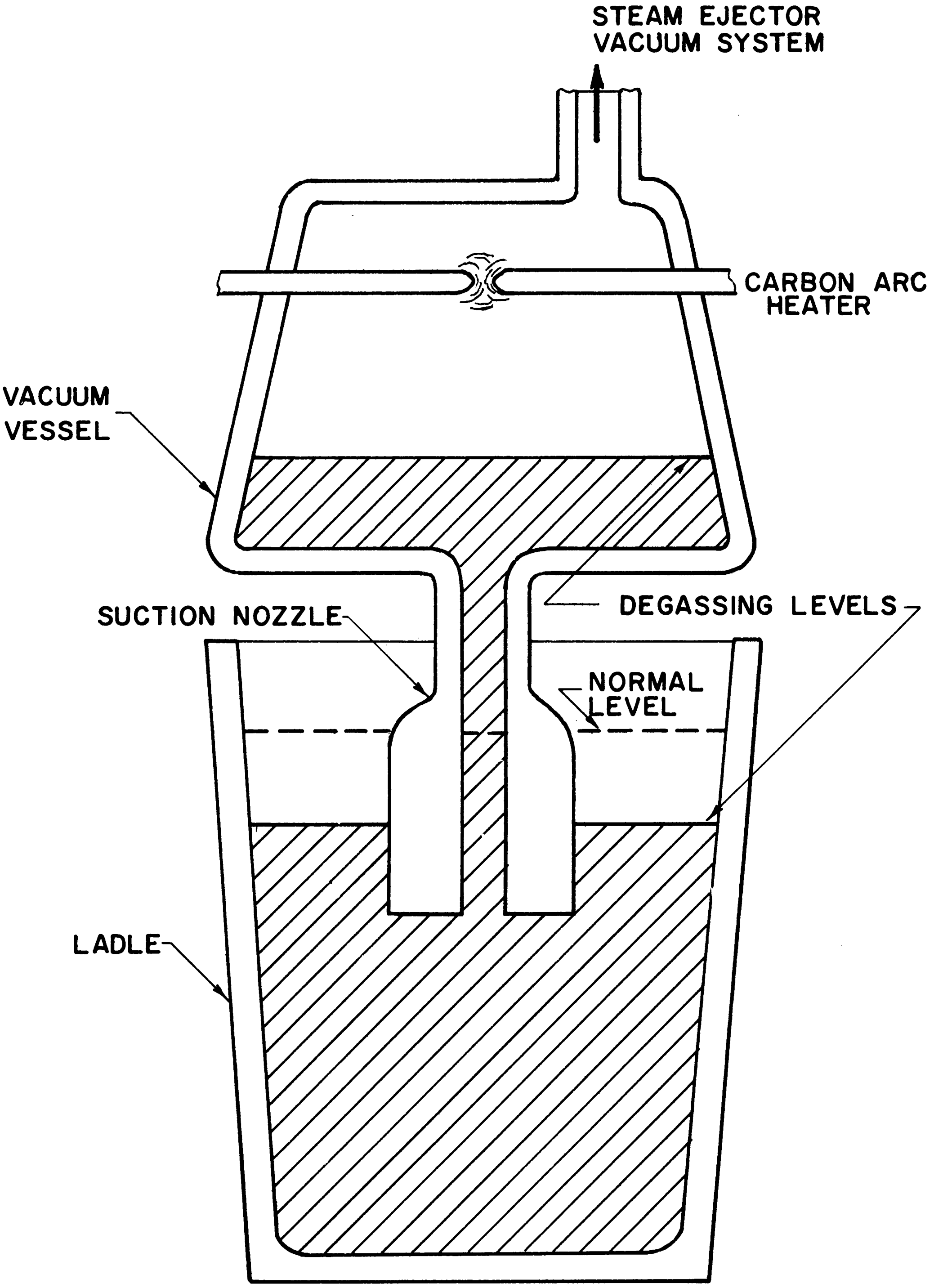

Figure V-1. Schematic View of Dortmund - Hörder Hüttenunion Vacuum Treating Process.

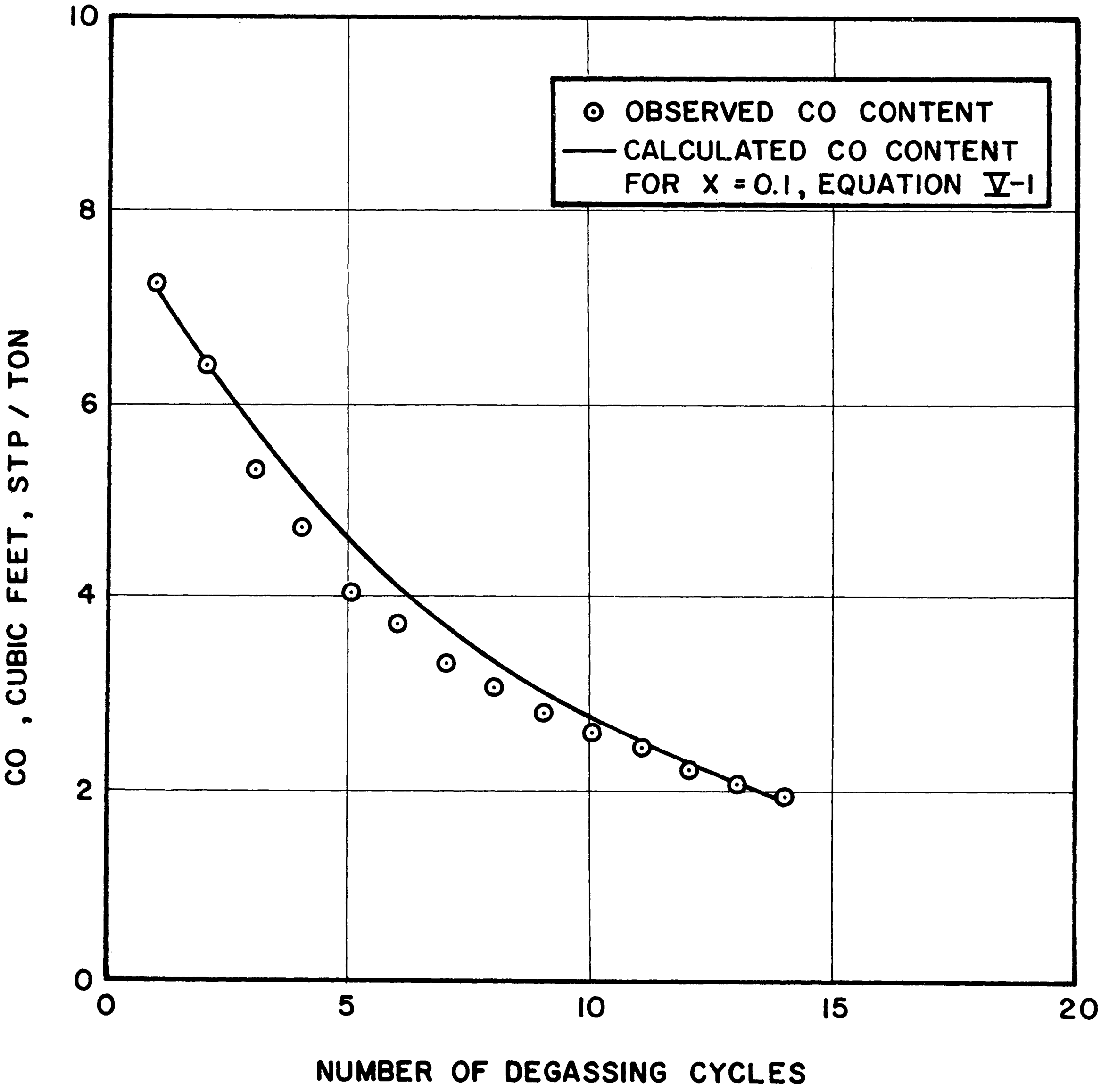

Figure V-2. Removal of CO from Liquid Steel by DHHU Vacuum Treating Process.

The success of the assumptions used to predict the performance of the Dortmund-Hörder degassing process should not be taken as a justification for their use in all cases. It should serve, however, to indicate the possibilities which exist for the process designer who is aware of the behavior of metallurgical processes and of the limitations of idealized treatments of those processes.

Heat Balance

The heat balance is founded on the mass balance and may be determined using the principles outlined in Chapter II. The difficulties encountered in specifying a complete enthalpy balance for a process often arise from problems encountered in the mass balance, i.e., composition and mass of streams entering or exiting the process. The lack of accurate thermodynamic data often hampers the writing of a reliable heat balance.

In the face of the difficulties indicated above, the process designer often lumps the error into a term called "heat loss" which includes in addition to the radiation and convection losses from the physical system, the cumulative errors in the other terms in the heat balance. It should be noted that the heat losses are quantities which may be calculated with a reasonable degree of accuracy in many cases. Hence, a better procedure is to estimate the accuracy with which each term in the heat balance may be determined. Shifts in the process variables could then be evaluated with a clearer picture of the limitations on the calculated result.

Kinetics

The subject of process kinetics is briefly introduced here in order to complete the descriptive facets which make up the thermochemical model. The specific treatment and a discussion of the limitations of the several approaches to the kinetic description of processes is reserved until Chapter XXVII where specific examples will be introduced in connection with simulation of processes.

The factors which are of importance in describing process kinetics and the rate determining mechanisms which play a role in determining these kinetics have been outlined in Chapter IV. The difficulties arise in integrating these rate determining mechanisms into the overall behavior of the process, i.e., of providing some quantitative and limiting description of the entire process on the basis of the behavior of the many components and multitude of reactions which generally make up a metallurgical process.

There are three possible approaches to this problem. The first and most difficult being an attempt to summarize the kinetic behavior of the process in terms of the rate mechanisms of all, or more reasonably, of the two or three most important ones. This approach, although the one which is most correct, is usually limited by either the lack of data on the kinetics of the system or a limited knowledge of the combined behavior of several reaction paths which may be competing or interrelated in some other fashion. In a simple case in which a single transport process is rate determining, this approach is a highly satisfactory one.

The second and most promising approach from a commercial standpoint is the experimental determination of overall rate constants for the process. The determination of these rate constants is often difficult and requires the use of high speed computing equipment. If such constants can be determined for a range of operating conditions, the process dynamics may be specified with a relatively high degree of accuracy without precise knowledge of the behavior of the reacting components of the process. This approach is often made from a less rigorous standpoint, that of averaging the known process data and estimating a reaction path for the process. This approach is often a fairly accurate one but lacks dynamic response to variations in process conditions, temperature for example, since the reaction path is predetermined. It is however, a convenient assumption, and one which has some merit in predicting process behavior.

The third and final treatment of process kinetics is the rather weak but often unavoidable assumption that the reactions go to completion or reach equilibrium in the time alloted, i.e., the ideal process. The limitation of this approach is obvious. The designer is faced with the predicament of proposing a process for which he has no sound foundation from which to recommend a process cycle. When such a stand is taken with regard to the rate of operation of a process on the basis of previous experience with similar systems, the limitation is not a great one. It should be pointed out however, that further improvement in the process operation will undoubtedly rest on a knowledge of the kinetics of the system and that lacking it, efforts should be made to obtain it from actual operation experience at the earliest opportunity.

The importance of instrumentation and control cannot be overemphasized. The lack of suitable instrumentation can prevent an intelligent and informed operation of a process, and often at a strong economic penalty. Incorporated with the thermochemical model, and specifically related to its limitations and inadequacies, must be the requisite instrumentation and provisions for control of the process during its operating cycle. The thermochemical model can serve as a guide to design and operation, but it is its integration with imaginative and sound instrumentation and control that will permit significant advances in the process industries.

CHAPTER VI

EQUIPMENT DESIGN AND SELECTION

An important area in which the process metallurgical engineer will be required to make decisions is that of equipment design and selection. The replacement, improvement, or construction of new facilities for the operation of metallurgical unit processes is an activity which is constantly being carried out in an industrial organization. To make such decisions it is fundamental that the metallurgical process engineer be completely familiar with all aspects of the unit process including a knowledge of the raw materials, products, and intermediate constituents which may be present; that he know the process temperatures, pressures, and concentrations throughout the operation, as well as the physical characteristics and the chemical composition of the substances involved, and knowing these things and having in hand, energy and material balances, he will be able to make competent design decisions.

While it is not proposed here to go into the details of the design of high temperature processing equipment, a brief description will be presented of some of the factors which must be considered. The first decision which the design engineer must make is the size and type of unit in which the process will be carried out, and how that particular unit will integrate with the overall processing system. In general, since many variations are possible in the selection of equipment, it is often necessary to make an economic balance based on the operation of the process in the types of units under consideration. This economic balance will involve an analysis of the capital investment required, the operating overhead, and other factors which enter into the determination of the total cost of a given piece of equipment. The general design may depend upon several varying factors and often it is necessary to make a parametric study of the particular design possibilities in order to determine the optimum one. High speed computers are often of great assistance in performing such a task.

Once the size and type of vessel has been determined, decisions must be made, ones which are often not independent of the selection of the size and type of vessel, on the materials of construction. These decisions require that the specific characteristics of the process be known in complete detail in order that materials may be selected on the basis of their strength, which of course, is influenced by the environment and temperature involved, their corrosion resistance or resistance to attack by the substances with which they will be in contact and the economics of the particular materials which are possible choices. In the interest of economics, the materials of construction may vary throughout the piece of equipment in which a process is carried out. The particular materials selected being a function of those point conditions which exist in a given region of the process. An example in this regard is given in the construction of basic open hearth furnaces[1], where a basic lining is used for the hearth of the furnace, but in general, silica (acid type refractory) is used for the roof. Such a decision is based strictly on economics and may be modified according to current conditions. In the particular instance cited, consideration is now being given to basic roofs for open hearth furnaces. Improvements in the processes for the production of high quality alumina have significantly lowered its price and, although at the present time it is more expensive than silica, it may be chosen as a suitable material on the basis of greater life.

The selection of specific materials for the construction of equipment in which metallurgical processes are carried out is often an art. The process metallurgical engineer who is working in the area of equipment design will undoubtedly rely on previous experience and on the results of studies, both laboratory and plant which have been conducted with regard to interaction of various materials under different conditions of temperature, pressure and composition. The problem of equipment design is an expansive one and often it is difficult to arrive at a suitable solution for the problem of selecting the optimum equipment and conditions under which to operate the process. With due regard for this, it may be stated that one of the most important factors involved is a thorough knowledge of the unit process, itself, and it is toward this goal that the remainder of the text is devoted. Attention is called to the list of supplementary references below which treat in some detail the problems mentioned above.

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Part II

MATERIALS PREPARATION, TREATING AND HANDLING

CHAPTER VII

SINTERING

Sintering is a process employed to make fine materials useful by heating them to an elevated temperature such that the small solid particles in contact with one another adhere and agglomerate into large useful particles without the process of fusion taking place. Sintering of fine materials occurs as a result of the driving force of the excess free energy of the powder over that of the dense solid by virtue of the different surface areas for the two states. Considerable research has been carried out to determine the mechanism of sintering.(1,2)

The sintering of large quantities of material is often necessary in the operation of a metallurgical plant. This process provides an opportunity to use fines and often makes a particular process feasible by converting the fine materials available as charge material into a useful agglomerated form. Sintering is usually accomplished with the Dwight-Lloyd machine. A schematic diagram of a typical sinter strand is presented in Figure VII-1.

For several years BISRA (British Iron and Steel Research Association) has been investigating the fundamentals of industrial sintering processes.(3-7) It is principally from these sources that the following engineering design relations for industrial sintering processes is developed.

About 50 years ago Dwight and Lloyd devised their first continuous sintering machine to convert non-ferrous ore fines into a suitable size for further refining. The basic features and principles have

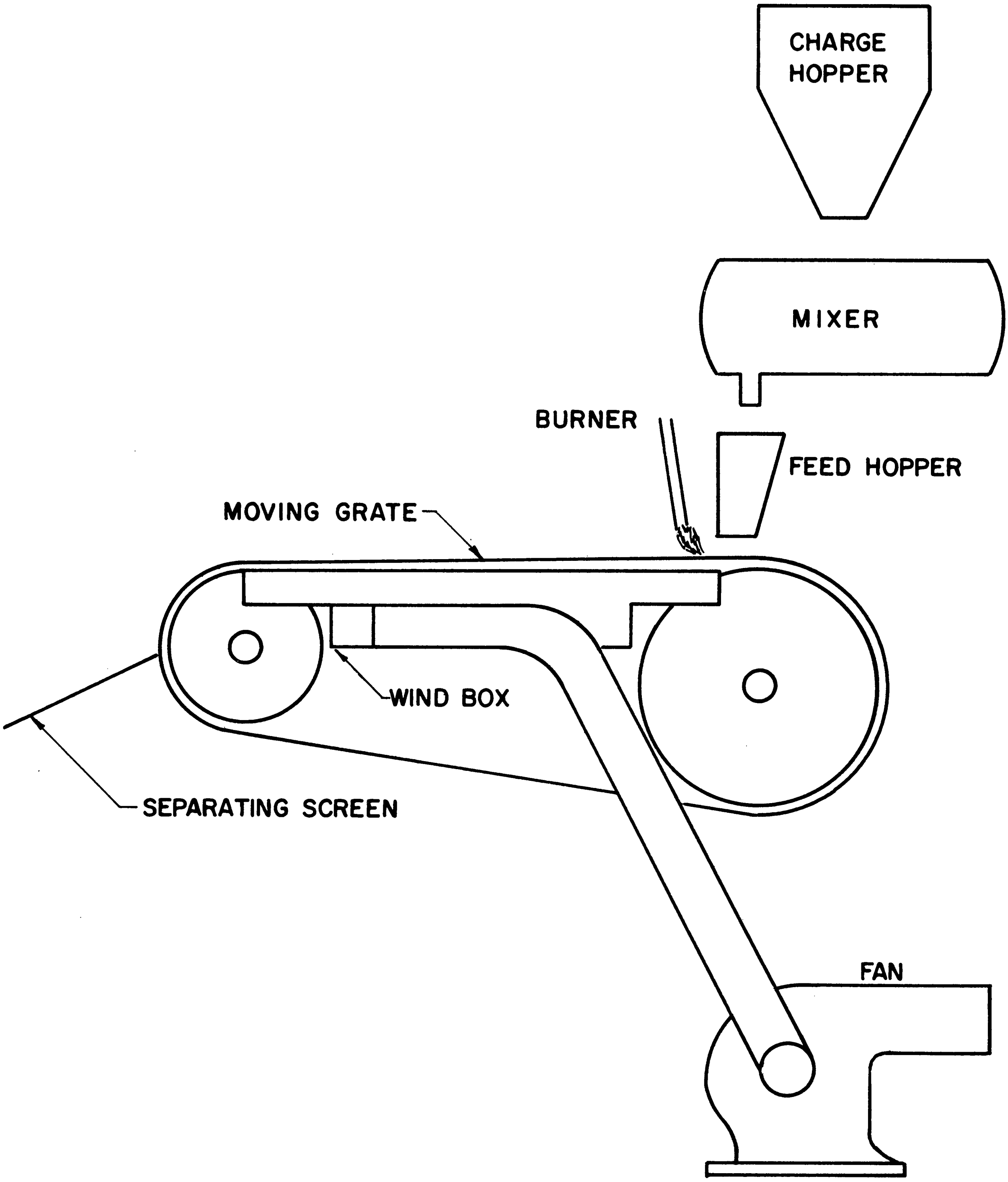

Figure VII-1. Schematic Diagram of Dwight Lloyd Sintering System.

not changed during those 50 years. Originally, for copper ores, sulfide fines were distributed in a thin layer along a traveling belt made up of grates. They were ignited and the sulfur was burned out of the ore as air was drawn through by large fans. The fines fused together forming a strong sinter cake which was desirable for reverberatory or blast furnace charging. The basic difference between the above process and the process used for ferrous ores is the self-contained fuel of the copper-bearing sulfide material. In the ferrous process carbon in the form of coal or coke has to be added to obtain a burning process.

As shown in Figure VII-1 the material for sintering is taken to a primary mixer. This mixer mixes the fines and added fuel and perhaps water, depending upon the state of preliminary agglomeration desired. The mix is then charged onto the moving belt of the conveyor where it passes under a set of flame nozzles which ignite the bed. The fuel burned in these nozzles is usually blast furnace gas enriched with coke oven gas. Air is drawn through the burning bed by the suction system below and at the end of the strand the sinter drops off the pallets onto a static screen where the large particles are taken off and the smaller ones are returned to the sintering process as recycle.

Heat Balance

In computing a thermal balance for the sintering process one needs only to account for the reactions taking place during sintering, particularly the burning of the fuel, the sensible heats of the input and output streams and the estimated heat losses during the process. Such a balance is presented in Reference 8 for the sintering of a lead ore. The fuel requirements to provide a normal temperature distribution down the bed for a number of sintering mixes are shown in Table VII-1, together with the net thermal requirements which may be seen to be relatively independent of the material to be sintered. The net thermal requirement has been obtained by subtracting the heat needed for endothermic reactions from the heat input of the coke and dividing the resultant figure by the residual weight of the solid. The fuel requirements given in Table VII-1 are for experimental materials. It is expected, however, that the actual metallic bearing ores which would be used in industrial practice have similar characteristics.

The optimum fuel requirement varies slightly with different sintering mixes. One may account for this by consideration of the reactions which take place during sintering. The composition of the ore also determines the peak bed temperature or the temperature at which the sintering actually takes place. Variation of this peak bed temperature will cause a variation in the optimum fuel requirement. Variation in the carbonate or water content of the sinter mix will give a variation in the width of the hot zone, since the hot gases from the ignition process pass down through the bed, driving off the water vapor, and decomposing the carbonates. If the matching of the heat front, often taken to be the point at which the temperature rises above 100°C, and the flame front is different, the width of the hot zone will increase. This is illustrated in Figure VII-2 which shows the broadening of the heat front in the sintering of marble (C_aCO_3) caused by incomplete calcination in advance of the flame front. Combustion is delayed in this case, giving rise to a broader combustion zone and an increased specific air volume.

TABLE VII-I

Fuel for Normal Temperature Distribution in Sintering

Material	Water %	Coke %	Net Thermal Requirement BTU/#
Alumina	3	5	580
Mullite	3	5	580
Silica	3	4.5	523
	9	5	504
Alumino-Silicate brick	22	7.5	593
	32	9	558
	40	10.5	540
Al-Si brick 83% Marble 17%	20	8.3	665
Al-Si brick 67% Marble 33%	20	8.3	580
Al-Si brick 50% Marble 50%	16	8.5	593
Al-Si brick 33% Marble 67%	16	9	558

From: E. W. Voice and R. Wild, Journal of Metals, p. 105, 1958.

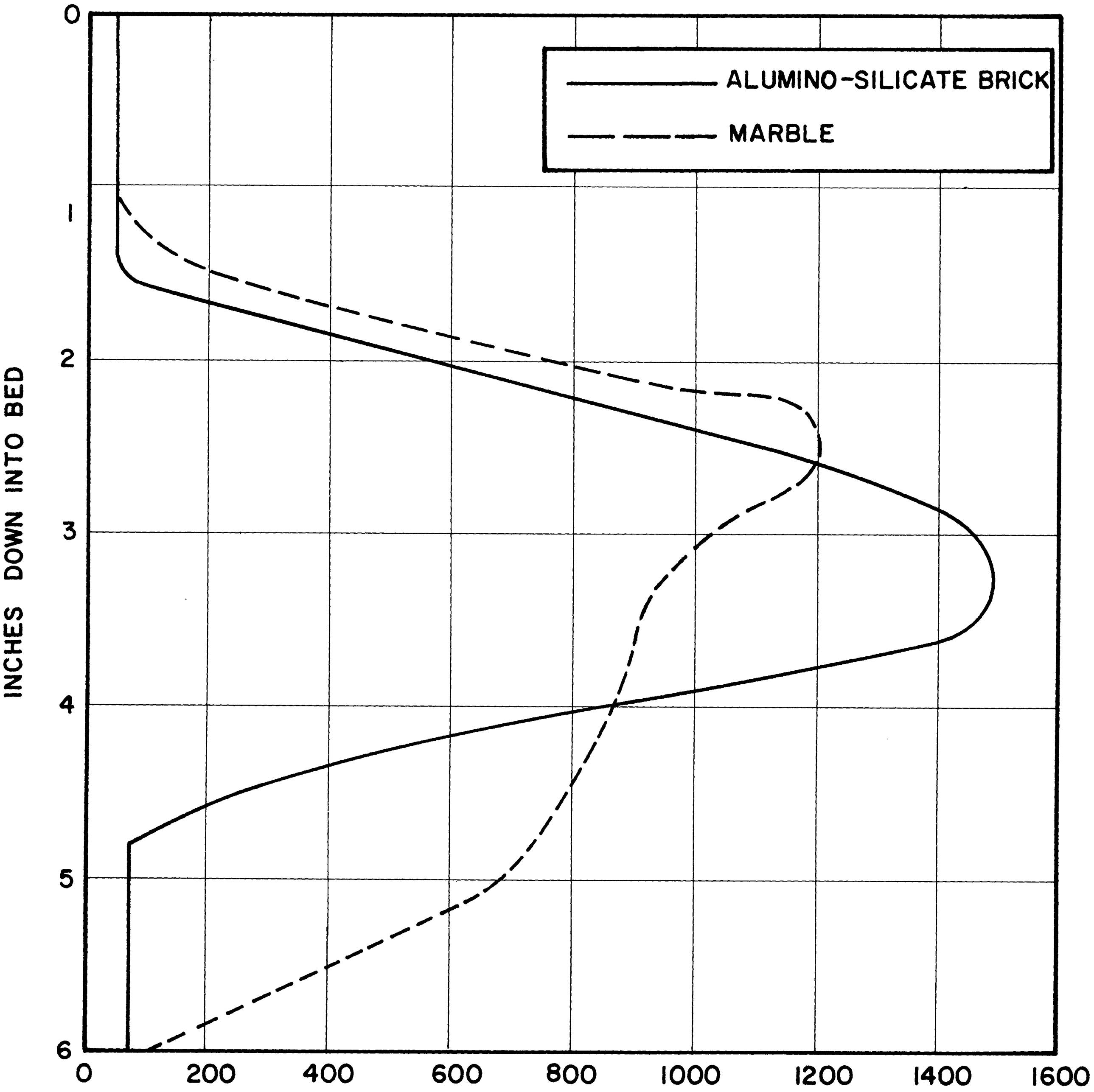

Figure VII-2. Temperature Distribution for Two Sinter Mixes When Combustion is Occurring Approximately at the Midpoint of the Bed.

It should be noted that the peak temperature is also reduced. Figure VII-2 also shows a reasonably well-defined flame front occurring during the sintering of alumino-silicate brick.

In addition to the variations in the amounts of water and carbonate present in different ore mixes, the specific heat will also change. Despite these factors, however, the net thermal requirement in general is about the same for a wide range of sinter mixes.

The high temperatures which are reached during sintering are possible because a hot zone travels through the bed and full use is made of heat recuperation between gases and solids. Thus the fuel has to supply heat for endothermic reactions, sensible heat to the solid material in the sintering zone, and make up for heat losses. Since the width and temperature distribution of the sintering zone are substantially the same for all materials, and the heat capacity is proportional to the weight of the material as are the heat losses, there is a theoretical basis for the experimental fact that the net thermal requirement is essentially independent of sinter mix.

Air Requirement

There is a definite rate of travel of the hot zone down through the bed which is independent of combustion. The heat generated in the top layers may arrive at a lower level in the bed in the same instant as combustion is taking place giving rise to an increase in the bed temperature; or it may arrive before or after combustion in which case it will widen the high temperature zone without raising the temperature reached. These two conditions may be termed matching and mismatching since the extent to which the heat front and flame front are coincident controls the temperature reached in the bed. Under optimum conditions, the combustion zone will be a narrow high temperature area.

The specific air volume required for the sintering process is controlled by heat transfer properties rather than combustion. Small additions of water to the bed delay the initial rise in temperature at any level but also increase the rate of rise above 100 °C. Large additions of water cause a very pronounced delay in the temperature rise above 100 °C, and thus a considerable increase in the volume of air required. The heat needed to evaporate the water and decompose the carbonates must be supplied by hot gases passing down through the bed; thus the presence of water and carbonate must delay the progress of the heat front to some extent. In the sintering process, the temperature in the combustion zone is between 1300 and 1500 °C. Thus the sensible heat of the gas leaving this zone is high and the delaying effect of endothermic reactions is minimized. Lower down in the bed, calcination liberates more gas at a relatively high temperature which also carries heat down through the bed. Still further down the bed, water evaporation takes place. Thus both carbonate and water in a sinter bed will increase the required air volume but the presence of water should have a greater influence.

The specific air volume is determined by three factors: (1) the mean air flow; (2) the rate of travel of the combustion zone through the bed; and (3) the bulk density of the mix. These factors are interrelated in such a manner as to produce a relatively constant air volume independent of sinter mix.

The specific air volume is controlled by heat transfer and increases in its requirements with increasing quantities of water in the mix. It should be noted that in commercial sinter plants considerable leakage occurs at the pallet seals so that the actual amount of air going through the bed is usually only half of that drawn in at the fan, and the plant operation should be designed on this basis. The minimum specific air volume requirement is approximately 25,000 standard cubic feet per ton.

Importance of the Width of the Combustion Zone

The combustion zone thickness depends on the extent to which the various fronts which travel down through a sinter bed are in phase. First, there is a water evaporation front which must keep ahead of the combustion zone or the bed will go out. Secondly, there is a calcination front which will cause a marked broadening of the combustion zone if it lags it. Finally, there are the heat fronts and combustion fronts. The extent to which these travel down the bed together will largely determine the width of the combustion zone. A narrow combustion zone will give high fuel efficiency and is a condition which should be aimed at in normal iron ore sintering practice.

Engineering Relations for Sintering Operations

The initial question facing the design engineer is the rate at which air may be drawn through the bed. This is determined by the bed permeability which is usually defined as the flow through a unit q of material under a unit pressure gradient, the units being self-consistent.

This definition leads to the following equation:(3)

$$p = \frac{F}{A}\left(\frac{h}{s}\right)^n \qquad \text{(VII-1)}$$

where

p = the permeability given in British permeability units,

F = the total sintering air flow in cubic feet per minute at 30 inches of mercury and 60°F

A = the grate area for sintering in square feet

h = the depth of the bed in inches (taken before sintering)

s = the suction under the bed

n = coefficient equal to 1 if the flow is streamlined or .5 if it is turbulent.

A number of experiments carried out on various sinter mixes before and after ignition have shown that the exponent, n, is independent of bed conditions and is approximately equal to 0.6. With change of pressure and temperature conditions, the permeability equation may be corrected, assuming ideal gas law behavior.

Air Flow Rate

The amount of air required per ton of material can be found by the following relation:

$$F = \frac{VI}{60} \qquad \text{(VII-2)}$$

where

V = the specific volume of sintering air per ton of raw material in cubic feet at 30 inches of mercury and 60°F

I = the input material rate in tons per hour.

Input Material Rate

The material input rate depends on the pallet speed, the available volume for the material, and its density.

$$I = \frac{h}{12}\left(v\,\frac{60}{12}\right)w\left(\frac{B}{2000}\right) \qquad \text{(VII-3)}$$

where

v = the strand speed in inches per minute

w = the strand width in feet

B = the bulk density of the feed in pounds per cubic feet.

The above equation gives the dimensions of the strand needed for any given input tonnage. Combining Equations (VII-1) and (VII-2) and rearranging terms, the input is found to be a function of the suction under the bed:

$$I = \frac{60\ WL\ p}{V}\left(\frac{s}{h}\right)^{0.6} \qquad \text{(VII-4)}$$

where

L = strand length in feet

This equation shows that the strand dimensions, specific volume and the permeability determine the input.

Output Material Rate

The output of a sintering machine is the difference between the input and recyle:

$$Q = I(y-c) \qquad \text{(VII-5)}$$

where

y = the yield as fraction of charged material which is discharged

c = the circulating load as fraction of charged material which is recycled.

Fan Horsepower

The power needed for the fan depends on the air flow that takes place through the wind legs, and the suction. The theoretical power can be obtained:

$$E_{th} = \frac{F}{6350} \qquad \text{(VII-6)}$$

where

E_{th} = the theoretical horsepower requirement for the fan operating on the sintering bed.

The actual horsepower is larger due to the leaks in the system, pressure losses in the air system, and the inefficiency of the fan.

Sintering Time

The time from entering the sinter machine until the sinter is discharged at the other end is:

$$t = \frac{12\ L}{v} \qquad \text{(VII-7)}$$

where t = the time in minutes to reach the peak wind box gas temperatures. From Equations (VII-3 and VII-4), the required length of the strand for sintering is:

$$L = \frac{v\ BV(h)^{1.6}}{288000p(s)^{0.6}} \qquad \text{(VII-8)}$$

Rearranging terms and combining Equations (VII-7 and VII-8):

$$t = \frac{BV(h)^{1.6}}{24000p(s)^{0.6}} \qquad \text{(VII-9)}$$

Equation (VII-9) shows that the depth of the bed greatly influences the sintering time.

Flame Front Speed

The rate at which the flame moves through the sintering material and the depth of the bed are the determining factors in the sintering time:

$$f = \frac{h}{t} \qquad \text{(VII-10)}$$

Experiments have shown that the flame front velocity is linear with time as indicated by Equation (VII-10). This equation may be rearranged in the form:

$$f = \frac{24000F}{V\ A\ B} \qquad \text{(VII-11)}$$

The flame front speed is shown to be dependent on the air flow which is a function of permeability, the limiting factor in the flame front speed.

The direct application of the derived equations above involve some knowledge of the process. Undoubtedly the design of a sintering operation will require laboratory or pilot plant experimentation. The above relationships, however, should prove to be extremely useful in permitting a prediction of the desired variation in controllable parameters that should accompany a change in sintering practice at a given industrial plant. The relationships derived apply as well to pelletizing processes.

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CHAPTER VIII

ROASTING - CALCINING - DRYING

A metallurgical unit process which is often very useful in an integrated operation is one which removes a volatile constituent from a solid material. The unit process may be termed roasting, calcining, or drying, depending upon the particular operation which is being carried out. These unit processes, however, are quite similar. The term "drying" is applied to the removal of water from a material. The water may be present either as a liquid or vapor or as chemically combined water. The nature of the process differs with these differing circumstances, but the basic operation is essentially the same. "Calcining" defines an operation in which carbonates are decomposed by heat, evolving CO_2 gas. "Roasting" is a similar process except that it involves reaction between the charged material and the combination gases. This reaction is one of oxidation in which sulfur is removed from ores in the form of SO_2. Roasting requires, in addition to the supply of hot-combustion gases, a free excess of air in amounts above those theoretically required for the roasting operation in order that each particle of ore may have sufficient contact with oxygen. In general, precise control of the amount of excess oxygen is necessary in order to prevent further oxidation of the roasted material. Roasting and sintering are unit processes which are often carried out simultaneously in a combined process "roast-sintering". In view of the fact that the process equipment and engineering approaches to these operations are quite similar, the remarks of this chapter will be restricted to one, calcination. It should be kept in mind, however, that the treatment presented here is one which may be suitably applied to all of these unit processes.

Lime and magnesia have long been important industrial materials. As is well known, the major tonage outlet for magnesia is in the refractories industry in which it is employed as "dead-burned grain magnesite." Lime is also used as a refractory material, since it has excellent refractory properties. However, it cannot be of service alone since exposure to the atmosphere after calcination will allow it to be slaked by the water vapor in the air, and fall to a useless powder. It should be noted that the use of burnt lime in the open hearth furnace has the advantage of decreasing the heat period and heat requirement. Calcination is carried out in many types of furnaces, both gas and electrically heated, and on hearths which are rotary, stationary or of the tunnel type in which the contents are carried through in small carts.

Of particular interest to the design engineer is the lime kiln performance, i.e., the process cycle described in terms of the time required for calcination and the thermal requirement.

Thermodynamics of Calcination

The reaction that occurs in calcining a chemically pure limestone may be expressed as:

$$CaCO_3 = CaO + CO_2 \qquad \text{VIII-1}$$

The equilibrium constant for Reaction 1 may be expressed as:

$$K = P_{CO_2} \qquad \text{VIII-2}$$

The free energy of decomposition may be expressed[1] as a function of temperature as:

$$\Delta F^\circ = 42{,}490-37.7T = -4.575\ T \log (P_{CO_2}) \qquad \text{VIII-3}$$

Equations (VIII-2 and VIII-3) may be utilized to predict the equilibrium pressure of CO_2 in contact with heated limestone, and the temperatures at which appreciable calcination of the limestone can take place.

Kinetics - Mechanism of Calcination

In addition to predicting the temperatures at which decomposition of the limestone can take place, it is necessary as well to consider the kinetics of the reaction. Although several experimental investigations have taken place to elucidate the exact manner in which the decomposition takes place, little success has been obtained in predicting a suitable mechanism for calcination. It has been found, however[2], that calcination of limestone takes place at a definite boundary plane, i.e., the boundary of two solid phases, one of lime (CaO) and the other of limestone ($CaCO_3$). This plane progresses from the surface of the piece of limestone being calcined toward the center at a definite rate and is maintained in about the same shape as the external surface of the stone. Other investigators have noted, however, that this particular mechanism does not always apply. In order to permit a precise description of the rate of calcination to be written in terms of the rate-limiting mechanism, further experimental investigation is necessary.

Based upon calcination data, Furnas[2] derived the following equation that can be used to determine the progressive penetration of the zone of calcination.

$$\log R = 0.003145T - 3.3085 \qquad \text{VIII-4}$$

Where R = rate of advance of the boundary line of calcination in centimeters per hour, T = temperature of the surroundings in degrees centigrade.

Equation (VIII-4) is purely empirical, and no theoretical basis should be attached to it. The equation has been derived on the basis of an approximation that the line of calcination advances at a constant linear rate and is dependent only upon the temperature of the surroundings, and is independent of the size and shape of the particle, the degree of calcination, and previous heating. Since the rate of penetration of the line of calcination is assumed to be constant throughout the entire period, the length of time required to calcine is directly proportional to the size of the piece.

Conley[3] performed a set of experiments on the effect of temperature on rate of calcination of high calcium limestone of cylindrical shape at one atmosphere pressure of carbon dioxide. On the basis of his data, he derived the equation

$$R = 0.005254T - 4.702 \qquad \text{VIII-5}$$

In view of the differing results obtained in these two investigations, it must be concluded that the rate of calcination is highly dependent upon the type and condition of stone as well as the conditions prevailing in the kiln. Undoubtedly, in practice it would be necessary to conduct a set of tests to determine the rate of calcination of the material to be processed before one specifies a set of operating conditions for a given calcination process.

Calcination time depends upon the prevailing external conditions of the stone, conditions which govern the heat supply to the stone surface. It is also a function of temperature of calcination, and of preheating and calcining reaction heat requirements. It is, in addition, a matter of the extent of external surface, of the exposure of the surface, of the thermal conductivity of the stone and lime, and the required calcining depth.

Heat Balance

Although the over-all heat requirement for the kiln may be specified by a heat balance for the process, it is often to the advantage of the designer to divide the kiln operation into several zones. Consideration of the heat requirement, heat transfer properties, and behavior of the material in each of these zones can lead to a better design and a more effective calcining operation. The zones depend upon the type of kiln, and in many cases can be considered as a preheating zone where the material enters the kiln and where the combustion gases are withdrawn, a combustion or central zone in which the actual calcining operation takes place, and at the far end of the furnace, a post-heating zone where the calcined charge is superheated or soaked at a specific temperature or where it may be cooled within the confines of the kiln. Often, to increase thermal efficiency of the kiln, recuperative preheaters are utilized to heat the incoming air and perhaps the fuel.

In improving the thermal efficiencies of the calcining operation, one is concerned primarily with heat losses. The loss of heat by transmission through the kiln structure, and radiation and convection to the surroundings from the structure surface, is generally less serious than the losses at the exit or entrance to the kiln. In computing the loss of heat through the surfaces of the kiln structure, one can generally assume that the inner temperature of the wall is at the same temperature as the operating process and perform a trial and error solution for convection and radiation losses from the exterior surfaces and balance this heat loss with the conduction loss through the refractory walls. There is a heat loss involved in the sensible heat of the hot lime which is withdrawn from the kiln. This is easily computed from the specific heat of lime and the temperature at which the material is taken from the furnace. Imcomplete combustion of the fuel is also a source of inefficiency in the calcination operation. Heat may be lost by incomplete combustion, both from combustible material leaving the plant in the form of ashes, and combustible gases lost out the stack. Suitable control of the fuel-air ratios and also a well-designed combustion system may be used to reduce these losses. It should be noted that adequate control of the draft is often an important factor in introducing sufficient air and fuel and providing a uniform distribution over the kiln cross section.

The greatest heat loss in the kiln operation is the loss of heat in gases going out the stack. The amount of heat in the exhaust gases may be calculated from the specific heat of the gases and their exit temperature. Often, this heat loss is a sum of many of the poor engineering developments that have taken place in the process itself. However, exhaust heat loss can be minimized with the use of recuperative preheaters.

The heat balance of the lime kiln may be written in the following manner:

Heat Input

The source of heat in any calcining operation is the fuel, generally coal or coke, and it is therefore necessary to know its calorific value and the total weight used. The heat input is then given by the product of the standard heat of combustion of the fuel times the pounds used.

Heat Output

Preheating limestone
Decomposing limestone
Further heating of lime
Heat losses:

1. heat loss due to radiation and convestion
2. heat loss due to imcomplete combustion
3. sensible heat of the exit gases
4. sensible heat of the hot lime
5. other possible heat losses which might include the sensible heat of solid products of combustion or a change in the ambient temperature of the kiln structure itself, etc.

Thermal Efficiencies

In discussing the thermal performance of a lime kiln, a common practice is to quote the ratio of lime produced to the fuel supplied for combustion. The true thermal efficiency of a lime kiln is expressed as the ratio of the heat theoretically required for calcination to the heat actually supplied to produce a ton of lime. The thermal efficiency varies from kiln to kiln and is a function of the stone, its size, the temperature of operation, and other factors which are involved in the contact between the combustion gases and the charge. The normal kiln performance is of the order of 25% to 35% efficient with a heat requirement of from 8-10 million BTU's per ton of lime produced.

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CHAPTER IX

HYDRO-METALLURGICAL OPERATIONS

Hydro-metallurgy is a phase of metallurgical-process engineering which deals with operations taking place in aqueous solution. These processes include solid-liquid extraction which is frequently referred to as leaching. Solid-liquid extraction is important in many phases of metallurgical engineering. A typical example is the recovery of copper from oxidized copper ores, which are generally low-grade ores containing less than 1.5 weight per cent copper, by extraction with solvents such as dilute sulfuric acid.

Extraction always involves two steps: (1) the contact of the solvent with the solid to be treated to transfer the soluble constituent to the solvent, and (2) the separation or washing of the solution from the residual solid. Liquid always adheres to the solids which must be washed to prevent either the loss of solution or contamination of the solids, depending upon which is the desired material. The complete process may also include the separate recovery of solute and solvent. A separate operation is usually involved which might be evaporation, distillation, electrolysis, ion exchange, solvent extraction or precipitation, the latter being one of the more common ones in the metallurgical industries.

An example of hydro-metallurgical operations is the extraction of gold and silver by cyanidation and precipitation of those elements from the cyanide solution with zinc. Leaching techniques are employed to obtain zinc oxide and copper oxide with acid, copper with ammonia, alumina with caustic soda, and uranium with acid or carbonate. The recovery of these solutes is then carried out by cementation or precipitation processes. Copper is recovered from acid solutions by cementation with iron, uranium and vanadium are recovered from acid or carbonate solutions by neutralization, and often metallic ions can be precipitated from aqueous solutions as insoluble sulfides.

In recent years, interest in hydro-metallurgical operations has been greatly intensified. This has been brought on in large measure by the necessity for turning to lower grade ore materials which must be concentrated in one manner or another before processing. Many of the new developments involve leaching and precipitation operations which are conducted at elevated temperatures and pressures.[1] The advantages for operating under these conditions are: (1) greatly increased rates of reaction, (2) favorable displacement of thermodynamic equilibria, and (3) the possibility of using certain gaseous or highly volatile reagents such as oxygen, hydrogen, and ammonia. Among the new processes which have resulted from the application of high-temperature and high-pressure techniques are direct leaching of nickel, copper, and cobalt sulfides with ammonia, carbonate leaching of pitchblend ores, leaching of certain sulfide ores with water, precipitation of metallic nickel, cobalt and copper from aqueous solutions of their salts by hydrogen reduction, and precipitation of uranium and vanadium oxides from aqueous carbonate solution by hydrogen reduction. Although there is a demand for advances relating to the physical chemistry of some of the older hydro-metallurgical processes, undoubtedly the employment of higher temperatures and pressures in conjunction with new extraction techniques will bring the greatest advances to the field.

Thermodynamics and Kinetics of Hydro-Metallurgical Operations

The engineer who is faced with the problem of designing a hydro-metallurgical operation may ask two questions: (1) Can a given chemical reaction or process be made to operate, and if so, under what conditions? and (2) What are the factors which determine the rate of the reaction, and how can this rate be controlled in practice? The answer to these two questions lies in an understanding of the physical chemistry of hydro-metallurgical processes. Thermodynamics attempts to answer the first question, and kinetics the second. Through the use of thermodynamics it is possible to define the equilibrium in a chemical system and to predict how the equilibrium will shift with changing conditions. An increase in the concentration or partial pressures of the reactants will shift equilibrium in the foreward direction while an increase in the concentration of the products will have the reverse effect. If any of the reactants or products are gases or highly volatile substances, the role of pressure becomes readily apparent, particularly, in view of the fact that many hydro-metallurgical operations take place in acid or basic solutions. Pourbaix has conveniently expressed the thermodynamics of these systems in the form of potential-pH diagrams. A discussion of this thermodynamic treatment has also been presented by Halpurn.[3] The thermodynamics of hydro-metallurgical operations can also be treated by the procedures outlined in Chapter III.

In general, hydro-metallurgical processes particularly leaching reactions, are conducted under conditions in which the thermodynamics are very favorable, that is, there is a large decrease in free energy associated with the desired process. The limitations are, therefore, largely of a kinetic nature. Most of the heterogeneous reactions of interest involve the following sequence of steps:

1. Absorption of gaseous reactants by the solution.
2. Transport of dissolved reactants from the main body of the solution to the solid solution interface.
3. Adsorption of reactants on the solid surface.
4. Reaction on the surface.
5. Desorption of the soluble products from the surface.
6. Transport of the desorbed products into the main body of the solution.

Step 1 could be rate limiting only in cases where gaseous reactants are involved. Usually however, a relatively fast gas absorption can be maintained by providing sufficient agitation of the solution and also a high partial-pressure of the gas phase.

The transport of a dissolved reactant to the surface (step 2) or of a product away from the surface (step 6) is more often rate limiting. In each case, the rate of transport to or from the surface is determined by the diffusion of the species across a boundary layer of thickness δ, immediately adjacent to the surface of the particle at which it is consumed or formed. Within this layer, the concentration of the diffusing species can be represented to a first approximation as a linear function of distance while on the solution side of the boundary layer, its value is the same as for the bulk solution. A treatment of this kinetic model has been presented in Chapter IV. The diffusion coefficient in aqueous solution is usually of the order of 10^{-5} cm^2/sec, and the boundary layer thickness is a function of the agitation. Its value normally ranges from about 0.05 cm in an unstirred system up to about 0.001 in a vigorously agitated one. Using these values, it can be shown that the maximum attainable rate in a diffusion-limited system is of the order of 10^{-1} mols per cm^2-hr, depending, of course, on the concentration of the diffusing reactant.

Processes which are rate-limited by diffusion can be speeded up by vigorous agitation of the liquid solution, by an increase in temperature, although the diffusion coefficient is usually characterized by a low-temperature coefficient corresponding to an activation energy between one and five kilocalories per mol, and also by maintaining a high concentration of reactant in the solution. Low rates of diffusion can result with localized accumulation of products, e.g. the formation of a precipitated oxide. The oxide, although soluble, might redissolve slowly and tend to passivate the surface where the reaction is taking place.

Steps 3 through 5, those involving adsorption, chemical reaction at the surface, and desorption vary greatly from system to system and do not lend themselves to consideration in general terms. In the event that a given hydrometallurgical process is rate limited by one of those steps, it would be necessary to make a specific investigation of the factors involved in order to adequately design the process in terms of the rate limiting mechanisms.

The Engineering of Solid-Liquid Extraction Processes

The equipment used for solid-liquid extraction may be classified according to the manner in which the first step is accomplished. A process in which the solid particles are kept in relatively fixed positions with respect to each other is denoted by the term "solid bed". It is possible that the solid bed remains fixed relative to the earth and that the solution moves through it, or it is also possible that the bed may be moved through the solution by means of a conveyor belt. Another type of solid-liquid extraction is the "dispersed contact". There is a variety of equipment which may be used in this case where the solids are dispersed in the solvent. In order that the particles remain in suspension, they must be extremely fine. However, in many cases, the suspension is maintained by agitation of the solvent, or the solids are moved through the liquid by means of screw conveyors, rakes, or other mechanical devices.

In general, the stationary solid bed extractor involves a minimum amount of handling and is often used where large amounts of material are required to be treated. For a more complete discussion of the particular equipment used, the reader is referred to any of the standard chemical engineering texts.[3,4,5]

The simplest method of operation for a solid-liquid extraction which includes the washing of solids is to bring all of the material to be treated and all the solvent into contact in one tank. This process is known as a single-contact batch operation. It is used, in general, only for small scale systems. The main reason being that a low recovery of soluble material is obtained. The total amount of solvent to be used can be divided into portions and the solid extracted in stages with fresh solvent. This method of operation is called simple-multiple contact. Although recovery is improved, the method is still not good because the product is relatively dilute in solute. This method is used where the soluble constituent is not a product. The most efficient technique, and the one most often used, is the multiple-contact counter-current operation. In carrying out a process in this manner, the product solution is last in contact with the fresh feed and the extracted solids are last in contact with fresh solvent. This process is characterized by a high solute concentration in the product stream.

Ideal Stage Concept

In most systems, the kinetics of leaching are not well defined, and consequently, calculations are based on the ideal stage. An equilibrium or ideal stage is defined for solid-liquid extraction as a stage from which the product stream leaving is of the same composition as the solution adhering to the solids, leaving the stage. Since this condition is not always fulfilled, the ratio of the number of ideal stages to the number of actual stages required to accomplish the same result is called the overall stage efficiency. The design engineer can compute the number of actual stages only if he has knowledge of, or some basis for estimating, the overall stage efficiency. Often a kinetic analysis of the problem can be of assistance.

In order to perform a calculation of the number of ideal stages the following conditions are assumed:

1. The system is composed of materials which may be treated as three components.
    a. Inert solids which are insoluble in the solvent or solids for which the solubility is known.
    b. A single solute which may be liquid or solid, or in the event that several solutes are involved, the interaction effects are known.

   c. A solvent which desolves the solute, but has no effect upon or is saturated with the solids.

2. The solute is not absorbed by the inert solid or in the event that it is, the relationships are known as functions of concentration and temperature.
3. The solute is removed by simple solution in the solvent without chemical reaction.

The computation of the number of ideal stages required is based on material balances. A knowledge of the quantity of solution retained by the solid and the definition of the ideal stage.

A mass balance is made about each ideal stage and this process is carried out until the solute or solvent exiting from a stream reaches the desired concentration level. The number of actual stages may then be obtained by dividing the number of ideal stages computed by the overall stage efficiency. Material balances can be made arithmetically but this approach is usually quite tedious. Graphical methods have been developed which greatly simplify the calculations, reducing error and also indicating clearly the variables involved and their effect on the operation. A detailed presentation of the arithmetic and graphical solutions for various types of solid-liquid extraction are presented in References 3, 4, 6, and 7.

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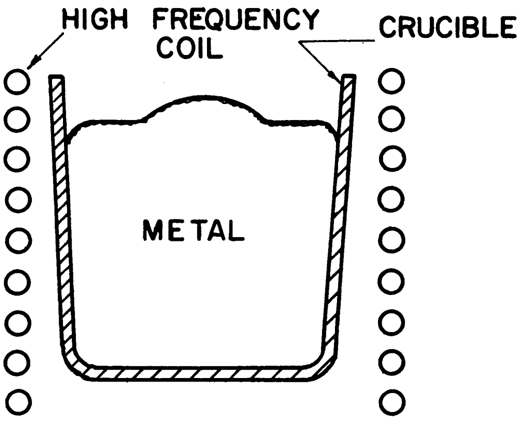
CHAPTER X

MELTING AND POURING

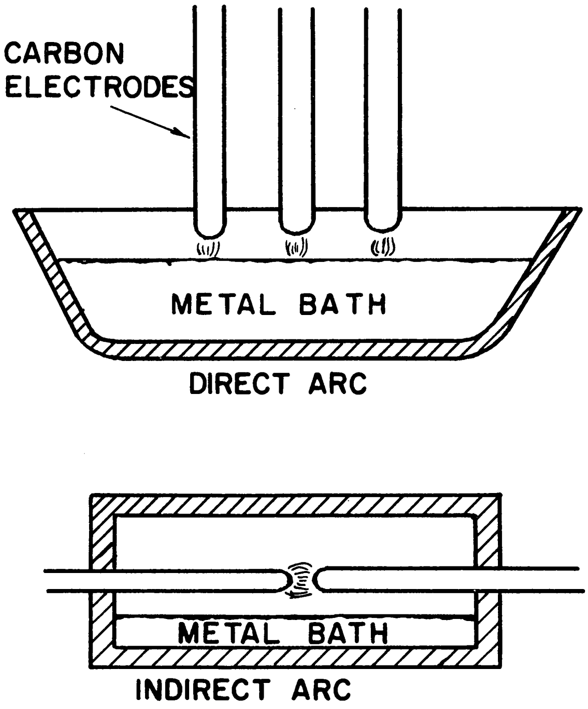
The kinetic advantages of a molten phase at high temperatures make it desirable to produce and refine metals in the liquid state. Since most metals are solids at ambient temperatures, it is necessary to supply them with heat to perform a melting operation. Subsequent to this, the metal is poured into and permitted to solidify in a mold of desired shape as either a casting or an ingot form. The material in this chapter deals with melting and pouring operations.

Melting Practice

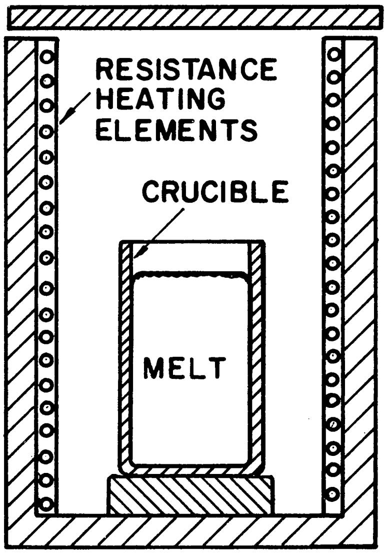
The minimum power required to raise a metal from room temperature to above its melting point is represented by the enthalpy increase which the metal experiences in going from the lower temperature to the higher. The actual power requirements, however, are much greater than this, and may be determined from a heat balance for the melting process. In writing such a heat balance, one must consider 1) the power input, 2) the sensible heat of the metal before and after the operation, 3) the sensible heat increase of the melting unit itself, 4) the heat losses, which include not only radiation and convection from the exposed surfaces of the melting unit, but also any heat removed by cooling water which is often used to protect critical areas of the melting unit. The heat balance is most conveniently written for a given period of time. The calculation of the power input depends upon the type of unit used. Several melting units are schematically represented in Figure X-1. Sketch A of that figure shows a type of melting unit which is quite



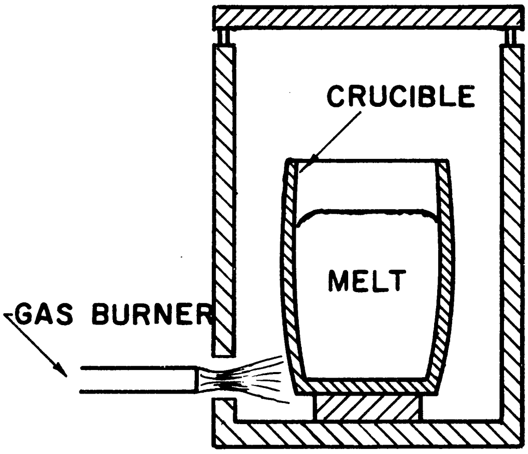
(A) INDUCTION MELTING



(B) ARC MELTING



(C) RESISTANCE MELTING



(D) GAS FIRED RETORT

Figure X-1. Melting Furnaces.

efficient in that the heat is generated in the metal. The alloy is placed within a coil which is supplied with a rapidly alternating current. The current flowing through the coil supplies the metal with a varying magnetic inductive force. This force produces electrical eddy currents in the metal which are dissipated in the form of heat. The power taken up from the coil by the metal is thus dependent upon the magnetic characteristics of the metal and its electrical resistance properties. Metals which are not easily melted by induction may be placed in a container made of a material such as carbon which is heated by the induction coil. If a reaction would take place between the metal and the carbon crucible, it is possible to surround a refractory oxide crucible with a cylinder which is heated inductively. The cylinder, usually a high melting point metal, is called a susceptor. A material which is often used under protective atmospheres for such applications is molybdenum which will withstand the high temperatures often involved in such an operation. Induction melting may be done in air, or in the case of metals which are easily oxidized or which are desired in a high state of purity, the melting may take place under a protective atmosphere or vacuum. Vacuum induction melting is often considered to be a refining operation, and a great deal of research effort has been expended in demonstrating that vacuum-melted materials are often superior to those which are air-melted.

Another type of melting unit using electric power is shown in Sketch B. This is known as arc melting and may be either of the direct or indirect type, depending upon whether the arc operates between electrodes and metal or between two electrodes in the system.

Large melting units used in electric furnace operation for steelmaking generally use three-pole direct arc systems which have melting capacities ranging up to 100 tons. In the case of indirect arc furnaces, the electrodes are often placed along the centerline of the furnace, and to avoid excessive attack of the refractory surfaces, the furnace is rotated to provide a cooling of the refractory surfaces by the liquid metal itself.

Resistance heating is often used to melt metals. There are a number of different types of resistance melting units, but in general the power is supplied by radiation from a heating element. For operation at low temperatures, high melting point metals are often used as heating elements. For slightly higher temperatures, the "Globar" furnace is often used, and for operation at even higher temperatures, carbon resistors may be employed. These electrodes are attacked by oxidizing gases and consequantly must be protected by an inert or reducing atmosphere, usually argon or carbon monoxide.

Melting furnaces often use low-cost fuel in the form of natural gas, fuel oil or powdered coal or coke. Sketch D shows such a furnace which may either be of the retort or reverberatory type. The economic advantages of using these types of fuels are often overcome by the deleterious effects of contamination. Coal and oil products generally contain sulfur which are undesirable in steels. Nevertheless, however, the major portion of the steelmaking industry in the United States is based on open-hearth operation, which is a gas or powdered coal fired reverberatory-type furnace as shown in Figure XIV-1. The power input to these furnaces may be computed from the heating value of the fuel and the heating value and sensible heat of the combustion gases.

Sensible Heat of the Metal

The sensible heat of the metallic charge may be calculated from a knowledge of the input and output temperatures of the charge and its specific heat. A more convenient method for handling such data is to tabulate the enthalpy increments for a given amount of metal, one pound mole for example. Table X-1 gives the enthalpy increments for several metallic elements.[1]

In order to compute the rate of heating, one may assume that the total heat transferred between the hot internal surfaces of the melting unit and the metal, or the heat transferred between the burning fuel or direct arc and the metal, takes place entirely by radiation. If such is the case, one must know the temperatures and total emisivities of the surfaces involved, and also the geometry of the heating system. The total emissivity of various surfaces have been tabulated[2], and geometrical effects have been summarized[3,4]. The rate of radiant heat transfer from a surface at T_1 to a surface at T_2 may be calculated from the relation:

$$\frac{dQ}{dt} = \sigma F A_1(T_1^4 - T_2^4) \qquad \text{X-1}$$

where σ equals the Stefan-Boltzmann constant, 1730×10^{-12} BTU/ft^2-hr-$^\circ$R., A_1 is the area of radiating surface 1, F is a dimensionless factor which accounts for the geometric relationship of the two surfaces to each other, and to other reflecting or refractory surfaces

TABLE X-1

HEAT CONTENT OF SEVERAL METALS[1]

$H_T - H^o_{298.15}$ cal/gm atom

Temperature °K	Aluminum	Copper	Iron	Lead	Magnesium	Zinc
298	0	0	0(α)	0	0	0
400	600	600	642	656	620	630
500	1230	1215	1318	1324	1256	1270
600	1890	1845	2044	2014	1920	1940
700	2580	2480	2832	3884(liq)	2610	4400(liq)
800	3310	3130	3703	4605	3330	5150
900	4060	3800	4682	5318	4095	5900
1000	7330(liq)	4490	5819	6024	7010(liq)	6650
1100	8030	5190	7135	6723	7810	7400
1200	8730	5895	8347(β)	7415	8640	
1300	9430	6615	9203	8100	9490	
1400	10130	10480(liq)	10059	8780		
1500	10830	11230	10915	9450		
1600	11530	11980	11771	10110		
1700	12230	12730	12939(δ)	10760		
1800	12930	13480	13914	11410		
1900	13630	14230	18658(liq)	12050		
2000	14330	14980	19714	12680		
2100	15030	15730	20774			
2200	15730	16480	21838			
2300	16430	17230	22906			
2400	17130	17980	23978			
2500	17830	18730	25054			
2600	18530	19480	26134			
2700	19230	20230	27218			
2800		20980	28306			
2900			29398			
3000			30494			

in the system, and the emissivities and absorptivities of the two surfaces, and T is the absolute temperature in ^{o}R.

Sensible Heat of the Melting Unit

The temperature increase of various portions of the melting unit must also be included in the heat balance. If the operation is carried out on a continuous or semicontinuous basis, the temperature distribution in the melting unit can be assumed constant. In this case, the term is negligible. One may also consider the change in temperature distribution of the melting unit, and attempt to estimate the sensible heat increase. In order to do this, it is necessary that one know the temperature distribution and also the enthalpy increments as a function of temperature for the furnace materials involved. A third approach which is often satisfactory, but less accurate, is to assign a factor to this quantity such that the sensible heat increase of the melting unit is represented by a fraction of the heat energy which is taken up by the metal. One may then multiply the sensible heat of the metallic charge by a factor which ranges from 1.1 to 1.5 for most cases.

Heat Losses

The principal heat losses in melting operations are the radiation and convection losses from the exposed surfaces. These losses may be computed by balancing the heat loss through the walls of the furnace with that lost by radiation and convection from the surface. This may be represented by the relation:

$$q_c = q_r + q_{conv} \qquad \text{X-2}$$

A trial-and-error approach to this problem is necessary where one solves the following equation for the interface temperature T_o:

$$q = \frac{kAm}{\Delta x}(T_i - To) = h_c A_o (T_o - T_s) + \sigma e_o A_o (T_o^4 - T_s^4) \qquad \text{X-3}$$

where T_i is the temperature of the internal surface of the furnace, T_o is the interface temperature between the outer surface of the melting unit and the surroundings, T_s is the temperature of the surroundings, k is the thermal conductivity of the furnace lining, Δx is the thickness of the lining, e_o is the emmissivity of the outer surface, A_o is the outer area of the melting unit, A_m is the mean of the inner and the outer surface areas of the melting unit, and h_c is the convective coefficient from the surface of the unit which may be taken on the average as being $0.3(T_i - T_s)^{0.25}$ for plane surfaces.

Other heat losses include the sensible heat of any gases or other products evolved from the unit during the melting operation as well as heat lost to cooling water which may be used to maintain low temperatures in certain critical areas of the melting unit. In the case where the metal surface is exposed directly to the surroundings, one may compute the heat losses on the basis of radiation from that surface assuming that black body conditions are approached by the surroundings. Samways and Dancy[6] have reported on the temperature drop of liquid metal between tapping and teeming and have statistically derived quantitative relationships based on plant observations.

Pouring Practice

Liquid metals are transported in metallurgical plants in ladles, which are cylindrically shaped vessels consisting of a steel shell lined with brick. The type of brick in most common use is fireclay brick. Ladles vary in capacity from 10 pounds to 300 tons. The operation of pouring from a ladle may take place in three ways. The heat may be lip-poured, bottom-poured, or a tundish may be used. Although lip-pour ladles are quite commonly used in plants producing small castings or pour large heats from one ladle to another (reladling), primary produced metal, particularly in the steel industry, is usually cast from the bottom-pour ladle. Figure X-2 shows a cross sectioned view of a bottom-pour ladle used for 200-ton open hearth heats. With this method of pouring, a stopper assembly acts as a valve to control the flow of metal through a nozzle at the bottom of the ladle. The size of the nozzle may vary in diameter from 1-1/4 to 3 inches, but it is of a length which is several times the diameter in order to provide a smooth, solid stream of metal free from turbulence. Nozzles are made from fireclay and the softening of the surface of the nozzle seat provides an adequate seal for the harder stopper-head. The stopper rod assembly shown in Figure X-2 consists of a steel stopper rod protected from the heat by a refractory sleeve and connected to an external control lever which permits the operator to start and stop the flow of liquid metal.

One of the most important factors affecting the surface of the ingot and the subsequent product is the rate of flow of the pouring stream and the resultant rate of rise of metal in the mold. This rate is determined by nozzle size, mold size, the temperature and fluidity of the steel, the height of metal in the ladle, and the erosion of the stopper and nozzle. The optimum pouring rate is determined by the grade of

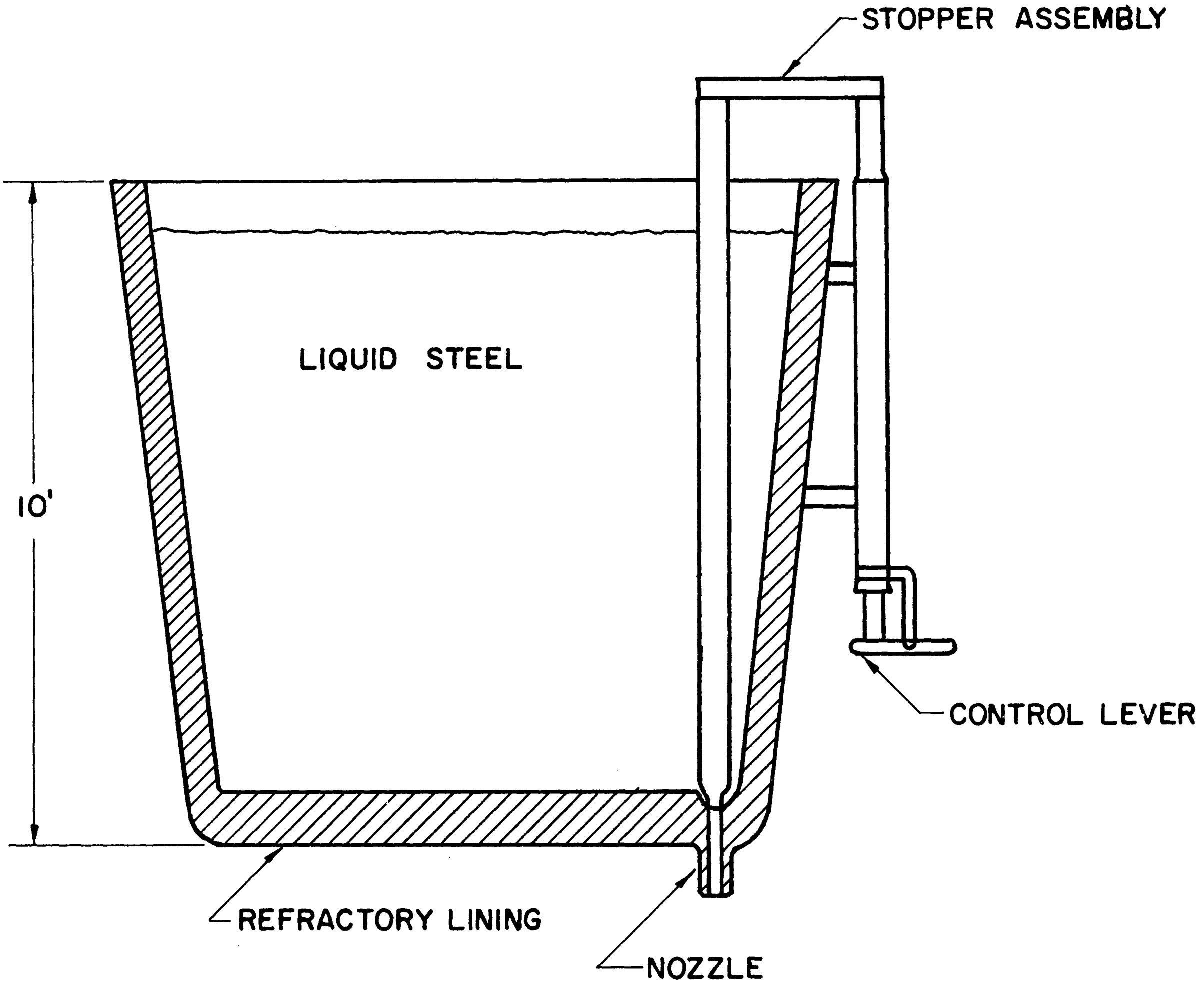


Figure X-2. 200 Ton Bottom-Pour Ladle.

steel, but is also dependent upon mold design and temperature of pour. In general, a slow pour minimizes ingot cracking but increases the tendency toward folded ingot surfaces. With fast pouring, however, the converse is true. The rapid rise of molten steel in the mold prevents a rippled surface. However, a large head is formed in the shell, which shrinks away from the mold wall and looses its support. Since the shell is very weak and cannot withstand the ferrostatic pressure of the liquid metal, it will rupture, permitting fresh liquid to break through to the mold surface. This produces a weakness in the ingot surface which may rupture on cooling or subsequent forming operations.

Rather than casting metal directly from the ladle to the mold, an intermediate pouring vessel may be used. Such vessels are called pouring baskets, pouring boxes, or tundishes. This method usually involves pouring from the tapping ladle into a vessel which has a nozzle leading into the ingot mold. Tundish or basket pouring is more expensive than conventional top pouring, but has the advantages that there is a greater opportunity for separation of non-metallic inclusions from metal, and there is also less splashing in the mold.

Bottom-Pour Molds

Some of the disadvantages of top-pouring mentioned above may be eliminated through the use of a bottom-pour mold assembly. The metal is cast into a runner system and finally emerges at the bottom of the mold through a special outlet. In bottom pouring, the metal rises steadily in the mold with very little agitation. Bottom-pouring is much more expensive than top-pouring, but is often used to insure optimum surface quality.

Rate of Pouring

The rate of pouring greatly influences the quality of a cast ingot. By considering the flow of metal through the nozzle of a bottom-pour ladle in terms of the flow equation, the rate at which metal is entering the mold at any time during the pouring operation can be estimated. In view of the fact that the nozzle erodes, one must have some relationship which indicates the size of the nozzle as a function of the amount of metal which has passed through it. Such correlations may often be obtained from plant data. If one also has estimates for the orifice coefficients and friction factors, the rate of pouring may be computed.

The gradual enlargement of the nozzle has an effect that is desirable, i.e., the rate of pouring does not decline gradually with the ferrostatic head in the ladle as it would if the nozzle opening remained constant. While the head of metal has been decreasing, the diameter of the orifice has been increasing, and the rate of pouring can remain nearly constant or even increase slightly. Since the rate of pouring has important effects upon the structure of the ingot, this may be an important aspect in the design of the pouring operation. Knowing the behavior of several materials which may be available for nozzles, the process engineer may select that one which provides a relatively constant pouring rate throughout the casting operation. Application of the generalized flow equation to the estimation of teeming rates from a bottom-pour ladle is illustrated by the following example problem.[7]

Example X-1

A steel ladle of the type shown in Figure X-2 contains 200 tons of liquid metal. The metal is poured out of the nozzle in the bottom into a series of molds below. The nozzle is 18 inches long and has an initial diameter of 2 inches. The nozzle erodes during pouring, however, and the eroded diameter is given by the relationship:

$$D_N = 2 + \epsilon N$$

where D_N is the diameter in inches, ϵ is the linear erosion coefficient, 0.006 inches per ton, and N is the number of tons of metal that have passed through the nozzle. The flow of liquid metal through the nozzle is characterized by the friction factor of the nozzle, the entrance coefficient, and the exit coefficient, which may be taken as 0.04, 0.20, and 1.0, and assumed to be independent of flow rate. The initial depth of metal in the ladle is 10 ft.

Calculate the rate of flow of liquid metal throughout the pouring operation, and comment on the suitability of the particular nozzle material.

Solution

The flow velocity can be calculated at any stage of the pouring operation by the flow equation, expressed in terms of the parameters of this problem.

$$\frac{g}{gc}(z_2 - z_1) + \frac{V_2^2 - V_1^2}{2\,g} + \frac{P_2 - P_1}{\rho} = -\bar{l}w - w$$

$$\bar{l}w = \frac{f_N\, V_N^2\, L}{2\,gc\,D_N} + \frac{\phi_N\, V_N^2}{2\,gc} + \frac{\phi_x\, V_N^2}{2\,gc}$$

where $\overline{lw}$ is the lost work caused by friction in the nozzle, f_N is the nozzle friction factor, and ϕ_N and ϕ_X are the entrance and exit coefficients, respectively. The work done on the system, w, is zero.

Selecting point 1 at the upper surface of the metal in the ladle and point 2 just below the nozzle, the pressure drop $(P_1 - P_2)$ is zero, and V_1, the velocity of the surface of the metal in the ladle is negligibly small in comparison to that exiting from the nozzle. Then,

$$- \frac{g}{gc} \left[10 \left(\frac{200-N}{200}\right) + L \right] + \frac{V_2^2}{2gc} = \frac{-V_2^2}{2\,gc} \left(f_N \frac{L}{D_N} + \phi_N + \phi_X\right)$$

$$V_2 = \left[(2\ gc) \frac{10\left(\frac{200-N}{200}\right) + L}{\left(1 + \frac{fL}{D_N} + \phi_N + \phi_X\right)} \right]^{\frac{1}{2}}$$

V_2, the exiting flow velocity in ft/sec can be converted to a flow rate by the relationship:

$$\overset{\circ}{N} \text{ (flow rate in tons per minute)} = \frac{V_2\ (60)\ D_N^2\ \pi\ \rho}{2000 \quad\quad 4}$$

Then:

$$\overset{\circ}{N} = \left[(2\ gc) \frac{10\left(\frac{200-N}{200}\right) + L}{\left(1 + \frac{fL}{D_N} + \phi_N + \phi_X\right)} \right]^{\frac{1}{2}} \frac{60\ D_N^2\ \pi\ \rho}{2000 \quad 4}$$

where $D_N = 2 + 0.006\ N$

Evaluating the last two expressions at the start of pouring:

$$D_N = 2 + 0.006 \times 0 = 2 \text{ inches}$$

$$\overset{\circ}{N} = \left[(2)(32.2) \frac{10\left(\frac{200-0}{200}\right) + \frac{18}{12}}{1 + (0.04)\frac{18}{2} + 0.2 + 1.0} \right]^{\frac{1}{2}} \frac{(60)(2)^2\ \pi\ 450}{(2000)(144)\ 4}$$

$$= \left[(64.4) \frac{11.5}{2.56} \right]^{\frac{1}{2}} \frac{240\ \pi\ (450)}{(2000)(576)} = 5.00 \text{ tons/min}$$

The expression can be evaluated at regular intervals of metal poured from the ladle in a similar manner, generating the curve shown in Figure X-3.

In view of the fact that one of the most important criteria for a successful pouring operation is a relatively constant pouring rate, the nozzle material of the example problem is highly suited to its application.

Also shown in Figure X-3 are the pouring rates for nozzle materials with various erosion coefficients used in the operation described in the example problem.

The results shown in Figure X-3 may be suitably averaged to provide an estimate of the total pouring time, using an expression of the general form:

$$t = \sum_{1}^{m} \frac{(\text{Tons Poured in Interval m})}{(\text{Average } \dot{N})_m}$$

The total pouring time of the operation described in the example problem is about 34 minutes. The digital computer[8] was especially useful in providing these results (See Chapter XXIV).

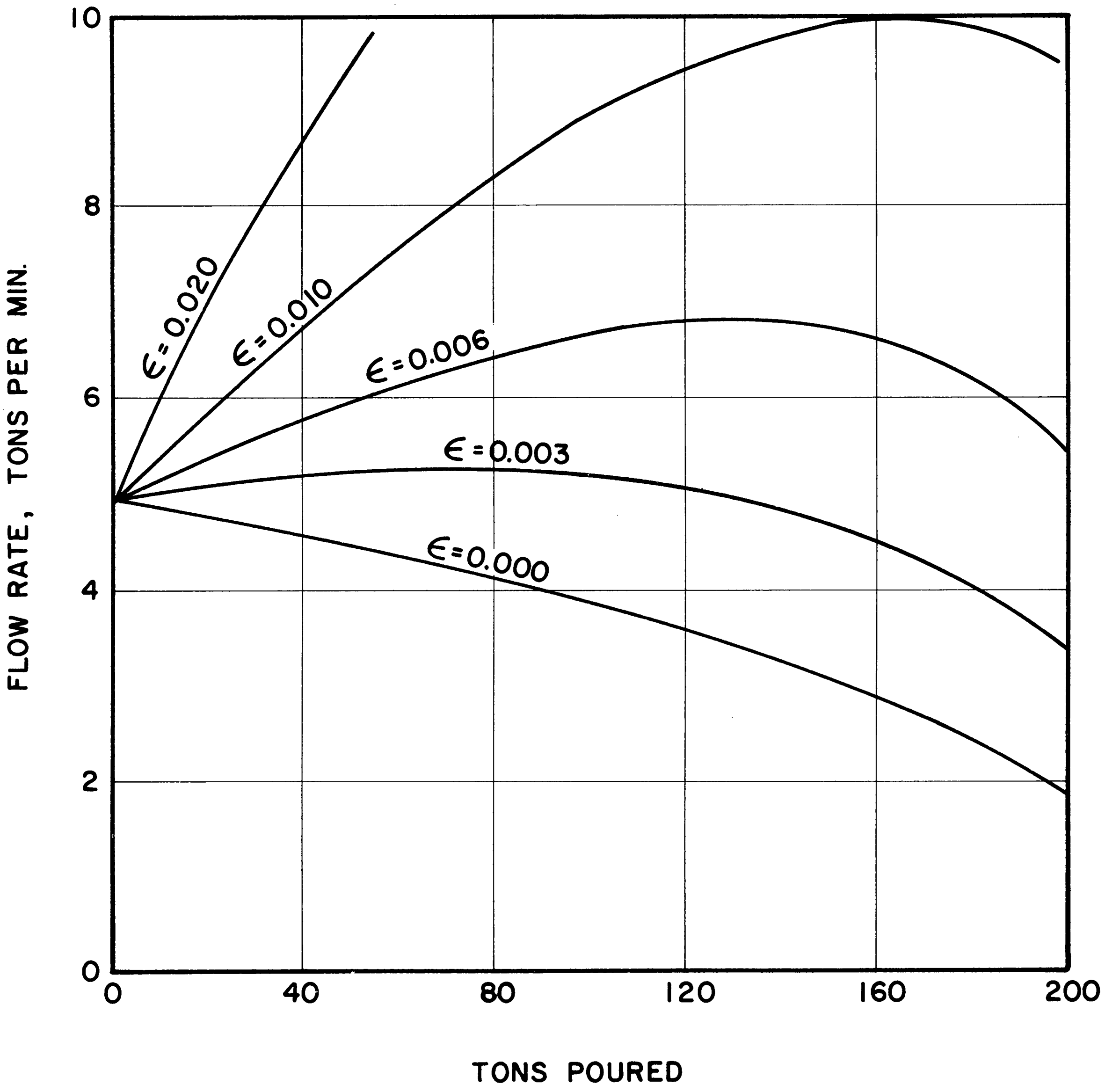


Figure X-3. Flow Rates from Bottom-pour Ladle for Various Nozzle Materials with Erosion Coefficient, ϵ.

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CHAPTER XI

CASTING AND SOLIDIFICATION

Following completion of the final refining operation, the liquid metal is poured from a furnace into a ladle. The liquid metal is then teemed from the ladle into molds and permitted to solidify. These solidified castings are called ingots. The eventual use of these ingots may be in any of several forming operations, including remelting and recasting in a desired shape. The forming operations which are used in the metallurgical industries are extensive subjects in themselves[1-6]. Consequently, the discussion in the present chapter will be limited to the casting of ingot shapes for use in further forming operations. The material presented here will be concerned chiefly with the rate of solidification, ingot structure, and some considerations of the continuous casting process.

Rate of Solidification

Flinn[6] has presented a mathematical analysis of the solidification rate of metal cast into a sand mold based on the work of Ruddle[7,8]. In this approach, it is assumed that the temperature of the finite(plane) boundary was instantaneously raised to and thereafter maintained at a temperature T_i at time $t = 0$. The temperature T at any point at a distance x from the finite boundary in a semi-infinte solid body is given by:

$$T_m = T_o + (T_i - T_o)\ \mathrm{erfc}\ (x/\sqrt{2\alpha t}) \qquad \text{XI-1}$$

where: T_m = temperature at distance x from mold wall into mold.

T_o = temperature at $t = 0$

T_i = mold-metal interface temperature

x = distance from mold wall

α = thermal diffusivity, $K/\rho c$

t = time

The rate of heat transfer across the mold-metal interface is given by the thermal conductivity multiplied by the temperature gradient. Differentiating Equation (XI-1) with respect to x, at $x = 0$:

$$\frac{\partial T_x}{\partial x} = \frac{(T_I - T_o)}{\sqrt{\pi \alpha t}} \tag*{XI-2}$$

and then:

$$\frac{\partial Q}{\partial t} \quad \frac{K(T_i - T_o)}{\sqrt{\pi \alpha t}} \tag*{XI-3}$$

If the freezing time depends on removing a certain amount of heat, Q, then:

$$Q = \frac{2K(T_i - T_o)\sqrt{t}}{\sqrt{\pi\alpha}} \tag*{XI-4}$$

Thus for a given metal and mold temperature:

$$Q = \beta\sqrt{t} \tag*{XI-5}$$

where β is a constant depending on pouring conditions.

If the freezing time depends on removing a given quantity of heat, then the thickness of frozen metal measured from the mold wall is given by:

$$d = \gamma\sqrt{x} \tag*{XI-6}$$

where γ is a constant. A similar result has been derived by Feild[9].

By considering an infinite plate, it may be shown that the total distance which the freezing plane must advance for complete solidification, one-half the plate thickness is also the volume to area ratio. Thus:

$$t = \gamma' (V/A)^2 \qquad \text{XI-7}$$

where γ' is a constant, and V/A is the volume to area ratio. This relationship has been shown to apply with reasonable accuracy to all casting geometries although it is only rigorous for infinite plates.

Ingot Structure

In addition to pouring conditions, i.e., temperature of the liquid metal, the nature and temperature of the mold, and its geometry, the rate of pouring, and other factors which affect the cooling rate, the most important factors which influence ingot structure are metal composition and gas evolution.

Effect of Rate of Heat Removal

A cast ingot will generally consist of three zones. Near the surface of the ingot the structure is very fine, randomly oriented grains. This region is called the chill zone and its structure is caused by a rapid rate of solidification during the early stages after pouring. Inside this zone is a second zone where the crystals are thin and elongated, perpendicular to the mold wall. This zone is called the columnar zone and is caused by relatively rapid heat removal giving rise to directional solidification and grain growth. Inside the columnar zone, the ingot has a granular structure in which the crystals are randomly oriented but are much coarser than in the chill zone. This zone is caused by a low rate of heat removal in the final stage of solidification. All ingots which do not involve gas evolution during solidification will show these three structures, the extent of the zones being a function of pouring conditions, composition, and average rate of solidification. The rate of solidification shows a large variation being nearly infinite at the mold surface and decreasing to a very small value near the center of the ingot. It is this variation in cooling rate during ingot solidification that causes the three structural zones described above.

Influence of Metal Composition

Since most liquid metals involved in metallurgical operations are not pure, they solidify over a temperature range with the first liquid solidifying having a different composition than that which finally solidifies. Most alloying elements lower the melting point of a pure liquid, and consequently, the first crystals of solid to form would more closely approach the pure major component than the composition of the bulk liquid. When the first crystals of solid form, they leave liquid next to them which is slightly less pure than the bulk liquid. The solidification of such a metal may then be visualized as crystals separating out which are more pure in the major component, and are separated from the bulk liquid by a film of liquid metal which is less pure than the bulk metal. Freezing may then proceed in any of three ways. (1) If the rate of solidification is very high, the less pure liquid solidifies so rapidly that the solidification process is indistinguishable from that of a pure liquid metal. (2) If the rate of solidification is slightly lower, the boundary layer of impure liquid may delay solidification slightly. (3) If the rate of solidification is very low, the bulk liquid beyond the impure film may reach its solidification point before the impure liquid. Free crystals will then form in the liquid and settle out to the bottom of the ingot. As a result of the change in solidification rate during the freezing of an ingot, all three types of freezing take place. These three freezing conditions produce the three zones described above.

These three zones are also characterized to a certain extent by segregation[10]. The segregation characteristics of an ingot are determined by its composition, its rate of cooling, and the tendency of the alloying element to segregate between liquid and solid.[11]

A killed steel ingot is characterized by two zones of positive segregation (areas in which the composition is greater than that of the average) and one zone of negative segregation (concentration lower than the average. These zones are shown in Figure XI-1. The conical zone of negative segration in the lower portion of the ingot is caused by the settling of free crystals which are purer and more dense than the bulk liquid. As the free crystals settle, they cause an upward movement of less pure liquid along the sides of the ingot near the solidification interface leading to positive segregation in this area. Similarly the V-shaped zones of positive segregation in the upper central portion of the ingot are caused by the movement of less pure liquid down into the ingot cavity by shrinkage during the final stages of solidification.

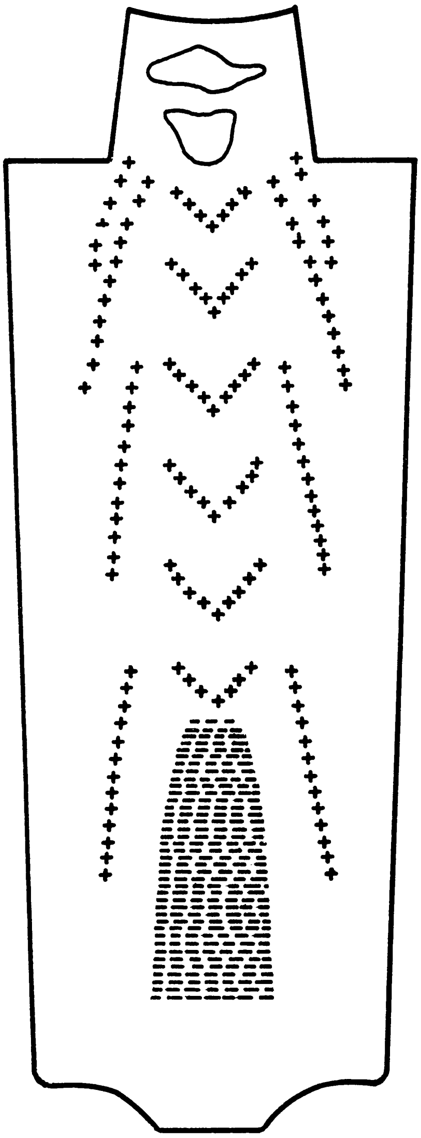

Figure XI-1. Segregation Pattern in Hot-topped Killed Steel Ingot.
+ Positive Segregation Zone
- Negative Segregation Zone

Examination of the equilibrium phase diagrams for most metallic systems reveals that the alloy content of the solid bears a constant ratio to the alloy content of the liquid in the region near the melting point. Chipman[10] calls this ratio k and has tabulated values of (1 - k), the segregation coefficient, for binary systems with iron. These values are presented in Table XI-1, where it will be noted that the values of k for a given element differ depending on whether the solid is gamma or delta iron. If the segregation coefficient is zero, this indicates no tendency to segregate since the alloy content in the solid and in the liquid would be the same. If the segregation coefficient is 1, however, this indicates that no alloying element will appear in the first solid to form, and consequently, this alloy would show extreme segregation.

Effect of Gas Evolution on Ingot Structure

The presence of gas in an ingot during solidification may not only change the physical nature of the ingot because of the prescence of blowholes caused by the gas, but may also affect the segregation tendencies of the ingot since the presence of a less dense gas phase causes fluid flow in the ingot during solidification. The presence of gas in an ingot is often an advantage, however, since the gas evolution will compensate for shrink and reduce or eliminate the ingot pipe giving a higher yield.

In the manufacture of steel, the carbon-oxygen equilibrium, and the influence of temperature on it, are of primary importance in the control of ingot structure by gas evolution. Carbon and oxygen react to form carbon monoxide whenever the equilibrium constant for

TABLE XI-1

SEGREGATION COEFFICIENTS FOR ALLOYING ELEMENTS IN IRON[10]

Element	Segregation Coefficient, 1-k	
	Delta Iron	Gamma Iron
Aluminum	0.08	
Boron	0.95	0.96
Carbon	0.87	0.64
Chromium	0.05	0.15
Cobalt	0.10	0.05
Copper	0.44	0.12
Hydrogen	0.68	0.55
Manganese	0.16	0.05
Molybdenum	0.20	0.4
Nickel	0.20	0.05
Nitrogen	0.72	0.46
Oxygen	0.98	0.98
Phosphorus	0.87	0.94
Silicon	0.34	0.5
Sulfur	0.98	0.98
Titanium	0.86	0.93
Tungsten	0.05	0.5
Vanadium	0.10	

the solution of the gas in liquid iron is exceeded. The reaction may be written

$$\underline{C} + \underline{O} = CO \qquad \text{XI-8}$$

where:

$$K = p_{CO}/a_C \cdot a_O \qquad \text{XI-9}$$

The equilibrium constant is thus proportional to the pressure of CO, which is a linear function of depth in the ingot mold. At atmospheric pressure near the top of the ingot, the equilibrium product would be one-half that which it would be at a depth of five feet in the ingot where the pressure is twice as great.

In practice, ladle deoxidation is used to reduce the oxygen to near the equilibrium level with the carbon present. As freezing proceeds, carbon and oxygen are concentrated in the liquid by the freezing out of pure crystals. This process results in gas evolution when the product of the carbon and oxygen activities exceeds that for the equilibrium value.

In a semi-killed ingot the concentration of oxygen is adjusted during the transfer in the ladle, and during the pouring operation in the mold, such that gas evolution compensates for shrinkage. As the steel shrinks during solidification the pressure is relieved, and additional gas is evolved. The top of the ingot then freezes over and gas formation in the lower part of the mold is controlled by the pressure.

Rimmed steels are characterized by rapid gas evolution which begins during the solidification of the chill zone at the mold wall. With the first solidification, marked gas evolution begins at the liquid-solid interface and the rising bubbles cause the liquid metal to move upward along the sides of the ingot and down the center. The motion of the liquid prevents the formation of columnar crystals and keeps the interior of the ingot at a nearly uniform temperature. Just inside the chill zone of a rimmed ingot is found a series of primary blowholes. The mechanism for the formation of these blowholes is described by Hultgren and Phragmen[12]. The formation of the elongated primary blowholes is caused by the formation of bubbles which are then swept away by the motion of the liquid. After the top of the ingot freezes over, enough impure liquid at the solid-liquid interface accumulates to start gas formation in much the same manner that it occurs in semi-killed ingots. This results in an interior series of spherical blowholes called secondary blowholes.

The upward motion of the liquid along the solidifying wall sweeps away impure liquid and mixes it with the unsolidified body of the ingot. This results in negative segregation in the rim zone of the ingot. There is then a large positive segregation in the upper central portion of the ingot, the last to solidify. Segregation in rimmed steel ingots has been discussed in some detail.[11,12,13]

The presence of other gases in steel ingots may cause blowholes, these being principally hydrogen and nitrogen. In the case of copper, the evolution of hydrogen and water vapor or SO_2 may also influence ingot structure, as hydrogen can in aluminum alloys. The control of gases in liquid metals is discussed in Chapter XXIII.

Continuous Casting

Continuous casting processes have received a great deal of attention in recent years, and have come into wide use in the casting of light alloy slabs and ingots. Application is now being made in the processing of copper and steel. The purpose of continous casting is to reduce ingot castings to a form which is directly rollable on finish mills. There is good indication that there should be improvements in yield, in surface condition, and in internal quality of ingots which are cast by this process.

The continuous casting of metal slabs involves the following operations: (1) delivery of liquid metal to the casting strand; (2) flow of metal through a distributor into the casting mold; (3) formation of the cast section in a water cooled mold; (4) withdrawal of the casting from the mold; (5) further heat removal from the casting; e.g. water spray beneath the mold; (6) cutting and removal of the cast bars. The rate of heat removal is the primary factor influencing the attainable casting rate. Obviously the casting rate could not be greater than one which makes it possible to remove the heat required for complete solidification prior to the time that the cast section is cut. Another more serious limitation on casting rate is the ability to develop a solid shell within the water cooled mold that can contain the liquid metal as the section leaves the mold. The governing factor here is the thickness of the shell emerging from the mold and this is determined largely by the rate at which heat is extracted in the mold. On this basis, then, the critical phase of the continuous casting process is involved in removing heat in the water cooled mold. It is on this phase of the operation that the following analytical discussion will be concentrated.

An analysis of the freezing of a continuous casting was made by Roth[13] who assumed that: (1) solidification does not begin until the metal reaches the mold (2) axial heat flow is negligible, and normal to the vertical axis, the temperature gradient is linear; (3) the surface temperature of that part of the ingot which is in the water-cooled mold is constant; (4) the metal is poured at the freezing temperature; (5) the thermal properties of liquid and solid metal are identical. On this basis the formula for the shape of the solidification front of a rectangular ingot is given as:

$$x = \frac{v \left[L\rho + \frac{1}{2} C_p \rho \left(\theta_f - \theta_s \right) \right] y^2}{2 K \left(\theta_f - \theta_s \right)} \qquad \text{XI-10}$$

where x = vertical coordinate measured from the top of the ingot mold, i.e. depth of liquid sump

y = horizontal coordinate measured from the side of the ingot, i.e., thickness solidified

v = speed at which ingot is moving vertically downward

θ_f = freezing temperature of metal

θ_s = surface temperature of ingot which is constant

L = length of mold

ρ = density of liquid metal (actually value averaged throughout mold volume)

This result implies that the instantaneous freezing rate is proportional to the horizontal thickness already solidified and predicts a wedge-shaped solidification front the sides of which are parabolic in section. The depth of the liquid sump should be proportional to v and to the square of the ingot thickness. The most serious errors in this treatment are likely to arise from assumptions 1 and 2 above. A review of this and other studies of the solidification of continuous castings has been presented by Ruddle.[14]

Savage and Pritchard[15] investigated the rate of heat transfer in continuous casting by measuring the heat transferred to a water stream passing through the cooled copper mold. They found that up to about 40 seconds after casting their results may be represented by the relation:

$$\frac{\partial Q}{\partial t} = 64 - 8\sqrt{t} \quad \text{cal/cm}^2 - \text{sec} \qquad \text{XI-11}$$

This equation gives for the average rate of heat transfer over a given period:

$$\left(\frac{\partial Q}{\partial t}\right)_{\text{ave}} = \frac{1}{t}\int_0^t \frac{\partial Q}{\partial t}\,dt = 64 - \frac{16}{3}\sqrt{t} \qquad \text{XI-12}$$

In the case of a continuous casting whose withdrawal rate is v cm per second, the mold length being L cm, t may be replaced by L/v so that Equation (XI-12) becomes:

$$\left(\frac{\partial Q}{\partial t}\right)_{\text{ave}} = 64 - \frac{16}{3}\sqrt{\frac{L}{v}} \qquad \text{XI-13}$$

The prediction of this equiation that the average rate of heat transfer increases with the casting velocity has been confirmed by experiment,[16] where it was also shown that the rate of freezing is proportional to the square root of t. The rate of freezing was found to be of the same order as that in an ordinary chill casting during the first stage of cooling, about 0.65 inches per minute$^{\frac{1}{2}}$. A large increase in the rate of freezing takes place during the second phase of intense cooling by water spray beneath the mold, q now being equal to about 8.44 inches per minute$^{\frac{1}{2}}$, a value much greater than that applying in chill casting. The plot of thickness frozen against the square root of t thus consists of two intersecting straight lines.

An investigation was performed at Inland Steel[17] on the continuous casting of low carbon steel. The thickness of shell emerging from the water cooled mold was estimated by measuring the outer slab temperature as the casting emerged from the mold. Using these temperatures and assuming a constant temperature gradient across a uniform solidified shell, the thickness of the frozen outer skin at the time the casting emerged from a 24 x 6-$\frac{1}{2}$ inch mold was estimated. The thickness of the emerging shell was found to decrease with increasing casting rate. The results of the investigation showed qualitative agreement with those of Savage and Pritchard.[15]

Although information at the present time is relatively limited, a heat balance for a continuous casting strand could be derived, based on a knowledge of the rate of heat removal during cooling in the chilled mold and in the water spray, and the amount of heat which must be removed which is specified by the metal and rate of casting. At the present state of the art, however, one would undoubtedly have to rely on pilot plant data in order to fully design a continuous casting process. The economics of continuous casting as well as a survey of the present status in a number of countries has been presented.[18]

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Part III

PRIMARY METAL PRODUCTION

CHAPTER XII

DIRECT REDUCTION OF METAL OXIDES AND HALIDES

As an introduction to the smelting techniques used for the production of metals from their oxides, halides, or other compounds, this chapter will be devoted to the thermodynamics of reduction reactions. As a general rule one may consider the relative stability of the compounds of two metals as being indicative of whether one metal may be used to reduce the other. For example, calcium oxide is a more stable oxide than the oxide of titanium; thus under suitable conditions the addition of pure calcium metal to titanium oxide will produce titanium metal and calcium oxide. The concentrations of the components in the phases which are present determine the degree of completion to which the reaction will go. The standard free energy difference for the particular reduction reaction indicates the degree of success which one might preduct would result from an attempt to perform such a reduction. The kinetics of reduction reactions are important and it is necessary that the process be carried out under pressure and temperature conditions which are favorable.

Unstable Oxides

The thermal decomposition of mercuric oxide has often been sighted as a classic example of the use of temperature alone for the reduction of a metal from its ore. Mercury occurs in nature principally as cinnabar (HgS) and since mercury is not easily oxidized the roasting of the sulfide mineral results in the formation of metal. The reaction is:

$$HgS + O_2 = Hg + SO_2 \qquad \text{XII-1}$$

The sulfide may also be decomposed by lime or iron according to the reactions:

$$4HgS + 4CaO = 4Hg + 3CaS + CaSO_4 \qquad \text{XII-2}$$

$$HgS + Fe = Hg + FeS \qquad \text{XII-3}$$

The kinetics of the above reactions require that they be carried out at temperatures above the boiling point of mercury. Consequently, means must be employed for the condensation of the vapor. Vapor pressure and enthalpy data for mercury are presented in Tables XII-1 and -2, respectively. These data may be used for computations involving the condensation of mercury vapors.

The use of reduced pressures for reduction reactions is often advantageous. In the case of the reduction of mercuric oxide by heat alone, the advantage of operating in a vacuum is obvious. The reaction involved would be:

$$HgO(s) = Hg(g) + \tfrac{1}{2}\,O_2(g) \qquad \text{XII-4}$$

The standard free energy change is given by the relationship:

$$\Delta F^\circ = -RT \ln K = -RT \ln \left[\frac{P_{Hg}\, P_{O_2}^{\frac{1}{2}}}{a_{HgO}}\right] \qquad \text{XII-5}$$

Metallic Reduction of Halides

The excellent mechanical properties, low specific gravity, and resistance to atmospheric corrosion, along with the fact that it ranks ninth in abundance among the elements in the earth's crust, created a strong interest in titanium. Great difficulty was experienced in producing ductile titanium directly from the oxide, and research led by W. J. Kroll led to a process involving the reduction of titanium chloride ($TiCl_4$) with metallic magnesium in a steel chamber. The tetra-

TABLE XII-1

MAXIMUM VAPOR PRESSURE OF MERCURY[1]
(In millimeters of mercury)

°C.	P	°C.	P	°C.	P
-30	0.000005	120	0.746	270	123.5
-20	0.000018	130	1.186	280	156.9
-10	0.000061	140	1.845	290	197.6
0	0.000185	150	2.807	300	246.8
10	0.000490	160	4.189	310	305.9
20	0.001201	170	6.128	320	376.3
30	0.002777	180	8.796	330	459.7
40	0.006079	190	12.423	340	557.9
50	0.01267	200	17.287	350	672.7
60	0.02524	210	23.72	360	806.2
70	0.04825	220	32.13	370	960.7
80	0.08880	230	42.99	380	1138.4
90	0.1582	240	56.85	390	1341.9
100	0.2729	250	74.37	400	1574.1
110	0.4572	260	96.30	*	*

[1] "International Critical Tables," III, 1928.

* 400-3100 °C.: $\text{Log } P = -\frac{3066}{T} + 7.752$

TABLE XII-2

HEAT CAPACITY AND HEAT CONTENT OF MERCURY[2*]

$\underline{T}$ °K	$\underline{C_p^\circ}$ Cal/°K-mole	$\underline{H_T^\circ - H^\circ_{298.15}}$ Cal/mole
298	6.69	0
300	6.68	12
400	6.54	672
500	6.48	1323
600	6.49	1970
629.9(l)	6.49	2165
629.9(v)	4.97	16302
700	4.97	16650
800	4.97	17140
900	4.97	17640
1000	4.97	18140
1100	4.97	18630
1200	4.97	19130
1300	4.97	19630
1400	4.97	20120
1500	4.97	20620
1600	4.97	21120
1700	4.97	21610
1800	4.97	22110

2 Elliott, J. F. and Gleiser, M. Thermochemistry for Steelmaking, I, Addison-Wesley, 1960.

* Referred to liquid from 298 to 629.9°K; ideal monatomic gas from 629.9 to 1800°K.

chloride of titanium can be produced in the liquid state by the action of chlorine gas on titanium carbide which is made by heating titanium concentrates with carbon in an electric arc furnace. The reduction process, called the Kroll process, provides for the introduction of liquid titanium chloride into a closed chamber, allowing it to drip on magnesium bars heated to 750°C in a reducing atmosphere. The reaction which takes place is:

$$TiCl_4 + 2\ Mg = Ti + 2\ MgCl_2 \qquad XII\text{-}6$$

The relatively high stability of magnesium chloride makes magnesium desirable as a reducing agent for the production of metals from their chlorides. Table XII-3 gives the standard free energy and heat of formation of several metallic chlorides.

The Carbothermic Process

The large energy change involved in the formation of CO or CO_2 and the insolubility of carbon in most nonferrous materials makes carbon a highly desirable reducing agent for the production of metals from their oxides. The retorting of finely ground, intimately mixed powders of an oxide material and carbon, resulting in the production of the metallic element and carbon dioxide gas, is termed a carbothermic process. The process is highly exothermic with most metals and often, as in the case of magnesium, produces a gas containing a metallic vapor. Unfortunately as the vapors cool the reaction reverses itself and the oxide is again formed. If, however, the gases are rapidly cooled from the maximum temperature, the metallic vapor may be condensed as a metal. A process based on this principle was developed by Hansgirg[2] for the production of magnesium. The carbothermic process

TABLE XII-3

FREE ENERGY FUNCTIONS AND HEATS OF FORMATION OF SEVERAL CHLORIDES*

	$(\Delta F - \Delta H_{298})/T$, cal/mole				
Compound	298.1°K.	500°K.	1000°K.	1500°K.	$-\Delta H_{298}$ Kcal/mole
AgCl	13.9	13.5	11.1(liq)	9.1	-30.3
$AlCl_3$	46	45(liq)			-166.8
AuCl	14	14	11		8
$BeCl_2$	32.6	32	28(liq)		112.6
$CaCl_2$	36.1	35.8	34.2	31.9(liq)	190.6
$CeCl_3$	56	55	54	49(liq)	260
$CoCl_2$	34.7	35.4	32.8(liq)	29.5	74
$CrCl_3$	55.7	55.7	52.4	49.6(liq)	132
$CuCl_2$	34	35	33		53.4
$FeCl_2$	31	30.9	28.8	24.3	81.9
$HfCl_4$	72	70			255
KCl	22.1	22.6	22.8	20.5(liq)	104.4
LiCl	17.4	17.8	17.5(liq)	16.6	97.7
$MgCl_2$	39.7	39.2	38.0(liq)	33.9	153.2
$MnCl_2$	32.9	32.8	30.6(liq)	26.4	111.6
NaCl	21.6	21.9	22.0	19.6	98.3
$NiCl_2$	34.8	35.0	33.9	31.2(liq)	73
$PbCl_2$	36.2	35.8	32.8(liq)		85.7
$SnCl_4$	56.8(liq)				127.4
$TiCl_4$	52.8(liq)	52.3			181.4
$ZnCl_2$	37.4	37	29.6		99.6
$ZrCl_2$	36	36	33(liq)		145

[*] Quill, L. L. The Chemistry and Metallurgy of Miscellaneous Materials, Thermodynamics. New York: McGraw-Hill, 1950.

has been used for the production of many metals. Unfortunately, however, in some cases the formation of a stable carbide prevents this process from being a practical one. One such case is that of aluminum where the formation of the carbide occurs when aluminum is held at high temperatures in the presence of carbon. The standard free energies of several metallic oxides and carbides are presented in Table XXI-1.

The Ferrosilicon Process

When calcined dolomite (a mixture of CaO and MgO) is heated under vacuum with ferrosilicon at about 1100°C, the magnesium is reduced and volatilized, and the SiO_2 formed in the reaction unites with the lime to form calcium silicate. This reaction forms the basis for the ferrosilicon process for the production of magnesium, usually referred to as the Pidgeon process. This process is typical of a number of reduction processes in which metallic elements are used for the reduction of oxides. Liquid aluminum may often be substituted for the ferrosilicon alloy. Calcium or sodium are often used for the reduction of uranium oxide. Although the standard free energy change may indicate that the reaction should go to completion, if two mutually soluble metallic elements are used resulting in the formation of an alloy, the activities, particularly of the primary reactant, are reduced, and the degree of reduction is limited. Provision in the process for making a separation of the metallic components may be of great assistance in carrying out the reduction process.

Gaseous Reduction Processes

The reduction of chlorides by hydrogen, or of oxides by hydrogen, carbon monoxide, or methane are processes which are being given considerable attention by process research and development groups. The reaction involved in such a process may be represented as:

$$MO + H_2 = M + H_2O \qquad \text{XII-7}$$

The thermodynamics of these reduction processes may be derived from the data presented in the tables of this chapter and Chapter XXI. Several techniques have been proposed for carrying out such reduction processes and in view of the advantages of a large surface area in carrying out gas-solid reduction operations, both packed and fluidized beds have been proposed. Although the engineering problems are more difficult in fluidized beds, the advantages of operating under continuous conditions has led to a higher interest in this type of operation. Consideration of fluidized bed reduction and the derivation of relations which are also applicable to fixed bed reduction processes are treated in the following chapter.

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CHAPTER XIII

FLUIDIZED BED REDUCTION

The fluidization of solids in a moving gas stream in order to carry out chemical reactions is becoming an increasingly important metallurgical process. Such a technique may be employed in operations involving calcination, oxidation, reduction, roasting, chlorination, sulfitization, and many other processes, including heat transfer and the physical movement of particulate bodies. The engineering design of such processes involves a knowledge of the pressure drop required to maintain fluidization, as well as the thermodynamics and kinetics of any reactions taking place in order that one can specify the mass and heat transfer taking place in the operation. Such operations are often advantageously carried out in several stages. In this case the details of each stage as well as the overall performance must be determined.

Pressure Drop

A pressure gradient which may be reasonably well defined is necessary to overcome friction associated with the passage of fluid upward through a bed of solid particles. The pressure gradient increases with flow rate. When the pressure drop approaches the weight of the bed over a unit cross-sectional area, the solids begin to move and fluidization sets in. This motion of solids occurs at superficial velocities which are far below the terminal free settling velocities of the solid particles. As the velocity of the fluid and the pressure drop are increased the bed continues to expand until the porosity (fraction of the bed which is void space) reaches unity.

These effects are shown in Figures XIII-1 and 2. In Figure XIII-1 the superficial velocity is shown to increase with increasing pressure drop until the point of fluidization is reached. At this point an increase in the superficial velocity does not involve further increase in the pressure drop. Figure XIII-2 shows that the porosity of the bed increases with Reynolds number up to the Reynolds number corresponding to the free settling velocity of the individual particles. At this point each particle behaves independently of other particles in the bed and the porosity may be assumed to be 1.

At the point of fluidization the forces tending to raise the particles are equal to the total weight, that is, the buoyant force (including the friction force) is balanced by the force of gravity of the particles. A force balance gives:

$$\frac{g}{g_c}(1-X)(LA)\rho_f + (-\Delta P_f)A = \frac{g}{g_c}(1-X)(LA)\rho_s \qquad \text{XIII-1}$$

where X = porosity of the bed

A = cross sectional area of the bed

L = thickness of the bed

ρ_s = density of the solid particles

ρ_f = density of the fluid

ΔP_f = pressure drop required for fluidization.

Solving for $-\Delta P_f$:

$$-\Delta P_f = L(1-X)(\rho_s - \rho_f)\left(\frac{g}{g_c}\right) \qquad \text{XIII-2}$$

The pressure drop equation may be used with other considerations to estimate the size of a fluidized reactor. The reactor must be large enough to accomodate the bed in its expanded fluidized state. The

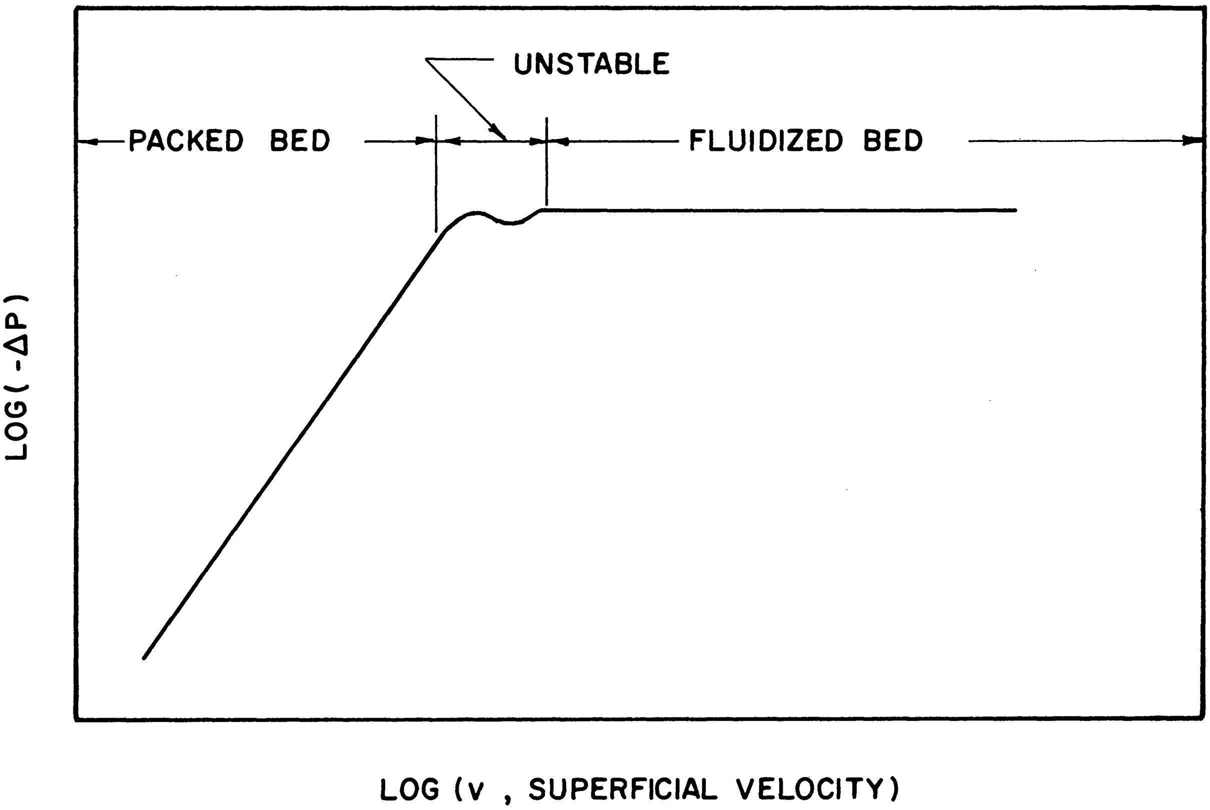

Figure XIII-1. Effect of Fluid Velocity On Pressure Drop for Upward Flow Through a Bed of Closely Sized Particles.

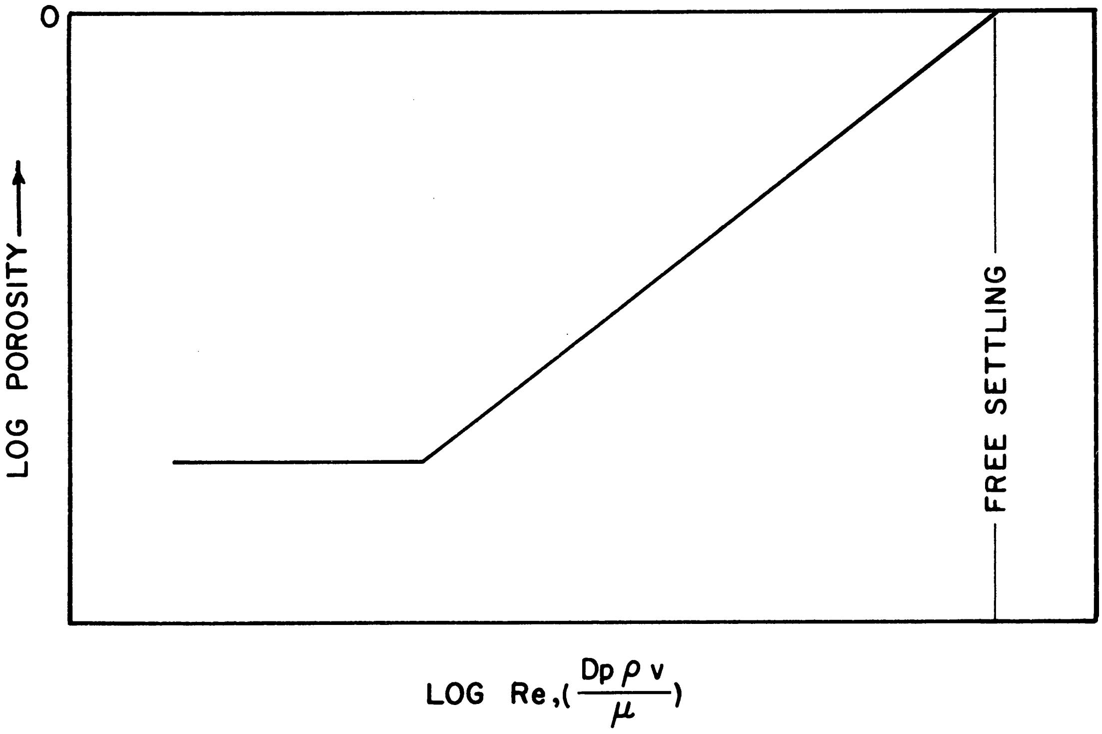

Figure XIII-2. Effect of Reynolds Number on Porosity for Upward Flow Through a Bed of Closely Sized Particles.

diameter of the bed may be determined from the mass velocity of the gas under operating conditions. The mass velocity of the gas must be such that the Reynolds number at which the system operates is above that at which fluidization occurs. The operating Reynolds number is often taken as 3 times the Reynolds number at the point of fluidization. The height of the reactor must be equal to the height of the bed in its expanded fluidized state. This may be determined from a plot such as shown in Figure XIII-2. The steps involved in the design of a fluidized reactor include: (1) Calculation of the Reynolds number at the point of fluidization. This involves a trial and error procedure since the friction factor is dependent upon the pressure drop in porous beds. (2) Choice of a suitable operating velocity above that corresponding to fluidization in order to fix the diameter of the reactor. (3) Construction of the plot of log Reynolds number versus porosity to determine the porosity of the bed at operating conditions and thus estimate the height of the reactor. This approach to the design of a fluidized bed reactor is outlined in Reference 1.

Process Thermodynamics

Thermodynamic calculations should be performed on the reactants and expected products of the fluidized bed reactor in order to determine whether or not the process is feasible, and if so, at what temperature the operation should be carried out. Several processes have been proposed involving the reduction of iron oxides using hydrogen, carbon monoxide or mixtures of the two gases. In addition, processes of chemical reduction, thermopyrolysis or disproportionation of halides in a fluidized bed have been proposed for the production of Al, Be, B, Cr, Co, Cb, Cu, Ge, Hf, Fe, Mn, Mo, Ni, Si, Ta, Sn, Ti, W, U, V, and Zr. These processes are not restricted to halide and oxide feeds. Sulfides or other compounds which can be produced with a satisfactory degree of purity at a lower cost may be substituted. A thermodynamic consideration which is often more important in terms of the rate of the process is the fact that several reduction steps occur. For example in the case of iron, a process might be carried out advantageously with several stages which would involve one for drying and conversion of Fe_2O_3 to Fe_3O_4, a second for reducing Fe_3O_4 to FeO, and a third for the final reduction of FeO to Fe. An equilibrium diagram for the systems Fe-O-H and Fe-O-C are presented in Figure XIII-3. The gas composition of either CO/CO_2 or H_2/H_2O required for a reduction step in converting the iron oxide to a lower oxide or to pure iron may be determined from the figure. Similar diagrams may be plotted from equilibrium data in other gas-solid systems.

Material Balances

The material balances for a fluidized bed reactor can be written around each stage of the process, based on the fact that the gain of atoms by the gas stream equals the loss of atoms from the solid stream. This may be denoted as:

$$G(y_n - y_{n-1}) = S(x_{n+1} - x_n) \qquad \text{XIII-3}$$

where G is the mass of the gas stream, S = the mass of the solid stream, y_n = the composition of the gas leaving stage n, y_{n-1} = the composition of the gas leaving stage n-1 or entering stage n,

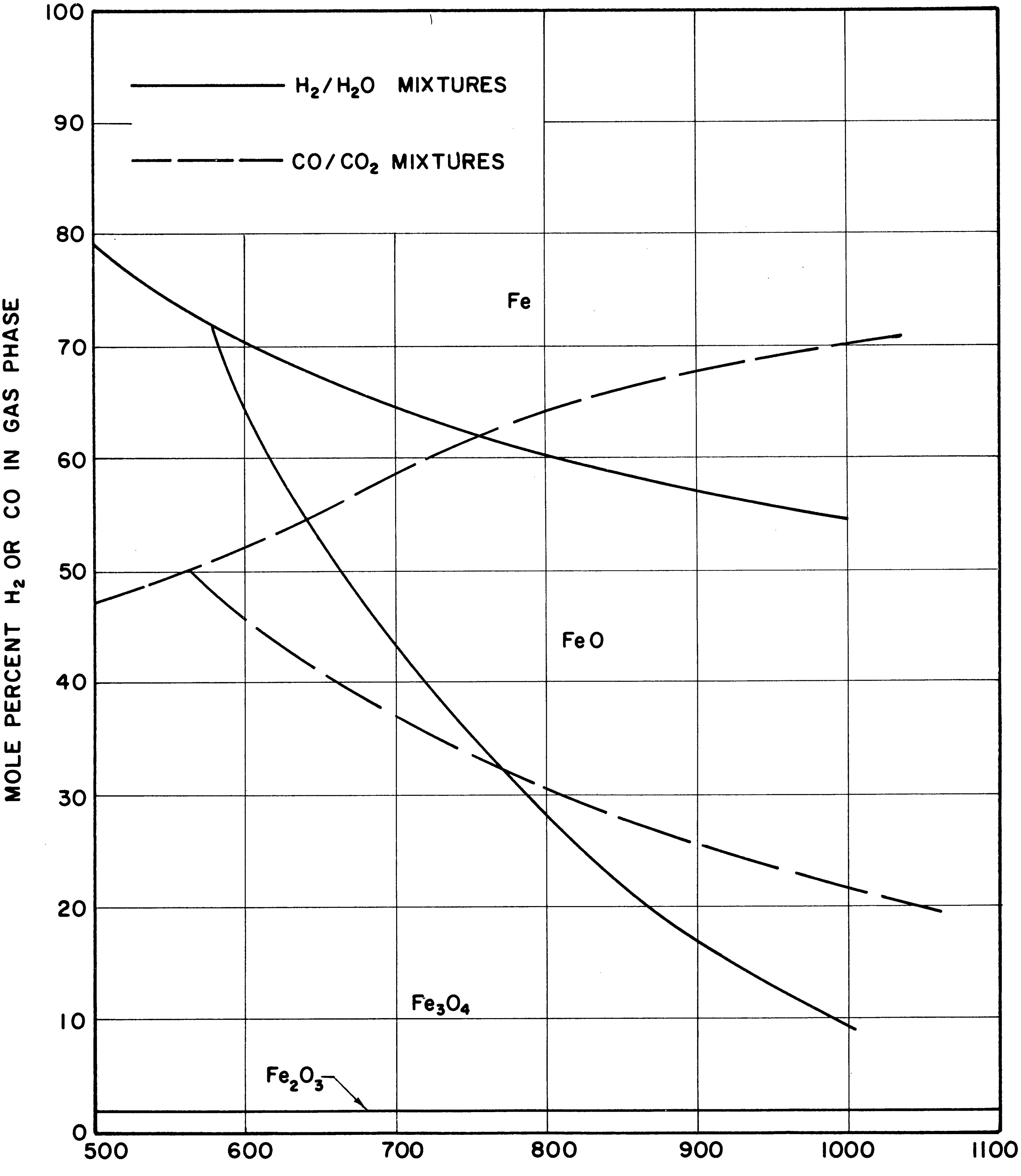

Figure XIII-3. Equilibrium in the Systems Fe-O-H and Fe-O-C.

x denotes similar nomenclature for the solid stream. This basic equation may be applied to a column of n stages where n may range from 1 to a very large number. It is apparent from Equation XIII-3 that a multistage operation is quite similar to that employed in hydrometallurgical processes, and a graphical technique similar to that mentioned in Chapter IX has been proposed.[2] This graphical technique is an adaptation of that developed by McCabe and Theile for use in distillation calculations.

Rate of Reduction

The kinetics of the reduction reactions taking place in the fluidized bed reactor may be controlled either by diffusion or by the rate of the chemical reaction. The controlling mechanism is determined by the system and the temperature of the process. Considering specifically the reduction of iron oxide by hydrogen, McKewan[3,4] showed that the rate of reduction per unit area was constant with time and directly proportional to the partial pressure of hydrogen. This indicated that the reaction was controlled at the oxide metal interface rather than by diffusion through the reaction product layer.

In view of the foregoing considerations a rate equation can be derived to fit the reported data. Consider a sphere of iron oxide of initial radius, r_o, and initial density, ρ_o. Assume that the rate of formation of uniform reaction product layer is proportional to the receding surface area of the remaining oxide. If W is the weight of that part of the original material that has reacted, then:

$$\frac{dW}{dt} = k\ A \qquad \text{XIII-4}$$

where k is a proportionality constant having the dimensions, $m\ l^{-2}t^{-1}$ and is a function of temperature, pressure and gas composition. From this it follows that:

$$r_o\ \rho_o\ f = kt \qquad \text{XIII-5}$$

where f is the ratio of the thickness of the reduced layer to the initial radius. Equation (XIII-4) states that at the oxide metal interface the amount of oxide reacting per unit area per unit time is constant or that the reaction interface advances at a constant rate.

The fractional reduction, R, is defined as the weight of oxygen removed divided by the total weight of oxygen originally present as iron oxide. The fractional reduction, R, bears the following geometrical relationship to the fraction thickness, f:

$$f = 1 - (1 - R)^{1/3} \qquad \text{XIII-6}$$

Substituting this value for f into Equation (XIII-5):

$$r_o \rho_o\ [1-(1-R)^{1/3}] = kt \qquad \text{XIII-7}$$

The same equation would apply to a cube whose side equals $2r_o$. The reduction rate for any particle whose shape is similar to a sphere or cube can be approximated by Equation (XIII-7). Equations can also be derived to fit other geometrical shapes.

The results of the above investigation were interpreted in terms of the theory of absolute reaction rates (Chapter IV). The specific rate constant, k', may be defined as:

$$k' = \kappa \frac{kT}{h}\ e^{\frac{-\Delta H^*}{RT}}\ e^{\Delta S^*} \qquad \text{XIII-8}$$

where κ is the transmission coefficient initially taken to be unity, k is Boltzman's constant, h is Planck's constant, ΔH^* is the entropy of activation, and ΔS^* is the entropy of activation.

For the case of hydrogen reduction of iron oxide the rate is directly proportional to the hydrogen concentration where the hydrogen concentration $[H_2]$ is expressed in mols per liter. Therefore the rate of reduction of iron oxide by hydrogen will be:

$$\text{Rate} = k_o \frac{kT}{h} [H_2] \, e^{-\frac{\Delta H^*}{RT}} \, e^{\Delta S^*} \qquad \text{XIII-9}$$

The data obtained in the foregoing investigation showed a break occurring at a temperature below which wüstite (FeO) is no longer stable. The interface in the high temperature range is FeO/Fe and in the low temperature range it is Fe_3O_4/Fe. The equations for the two ranges are:

$$\text{High Temp Rate} = 7.32\, T[H_2] e^{\frac{-15,300}{RT}} \quad gm/cm^2\text{-min} \qquad \text{XIII-10}$$

$$\text{Low Temp Rate} = 9.12\, T\, H_2\, e^{\frac{-14,900}{RT}} \quad gm/cm^2\text{-min} \qquad \text{XIII-11}$$

Another approach to the kinetics of reduction of a granular bed of iron ore was taken by Wiberg[5] and Edstrom[6] who showed that the reduction of iron ore in a gas stream tends to follow a first order reaction rate. The expression for this is:

$$\frac{-dc}{dt} = k_r\, c \qquad \text{XIII-12}$$

The term dc/dt is the rate at which oxygen is removed from the ore in pounds of oxygen per pound of iron per hour; c is the concentration of oxygen in the material in pounds of oxygen per pound of iron; k_r is the reduction constant in hours^{-1}. Collecting terms and integrating between c_o at $t = 0$ and c at time t:

$$\ln \frac{c_o}{c} = k_r\, t \qquad \text{XIII-13}$$

or the fraction of oxygen remaining at time t is:

$$f_o = \frac{c}{c_o} \quad e^{-k_r t} \qquad \text{XIII-14}$$

As a first approximation it may be assumed that the overall reduction rate of ore particles in a fluidized bed proceeds according to this type of equation. The actual value of the reaction constant, k_r, should be determined in a small scale reduction bed in which conditions would be typical of those in the larger unit which is being designed.

Residence Time

In view of the highly dynamic characteristics of a fluidized bed, mixing of the solid particles is assumed to be perfect. Several investigations[7,8] have shown this to be approximately true. With this assumption the residence time of particles entering a single stage can be determined. The mean retention time (θ) as defined below may be taken as a suitable measure of retention:

$$\theta = \text{quantity in system/rate of treatment} \qquad \text{XIII-15}$$

where θ is in units of time and the other quantities are in a consistent set of units. To estimate the retention time of solid particles in the reactor, let us assume at time t = 0 a small quantity, n_0, of tagged particles is added with the feed; let n = the number of tagged particles in the reactor at time t ($n = n_0$ when $t = 0$). The concentration in the reactor and in the exit stream at time t is n/V, where V is the volume of the system. The number leaving the tank in a time increment, dt, is then -dn which must equal the product of the effluent concentration, n/V and effluent volume, vdt, where v is the flow rate through the system. Thus:

$$-dn = \frac{n}{V} v \; dt \qquad \text{XIII-16}$$

Integrating, and noting that $n = n_0$ when $t = 0$:

$$\ln \frac{n_0}{n} = \frac{v}{V} t \qquad \text{XIII-17}$$

Since V/v is the mean retention time, Θ, defined previously and n/n_0 may be defined as r, the fraction still remaining in the system at time t, then:

$$r = e^{-\frac{t}{\Theta}} \qquad \text{XIII-18}$$

The fraction of the total number of particles discharging in the time interval from t to $t + dt$ is $-dr$; i.e., $-dr$ is the fraction of the particles with retention times between t and $t + dt$. Differentiating the previous equation:

$$-\frac{dr}{dt} = \frac{e^{-\frac{t}{\Theta}}}{\Theta} \qquad \text{XIII-19}$$

The normalized plot of $-dr/dt$ vs t in Figure XIII-4, based on this equation, shows graphically the distribution of retention times. The total area under this curve from $t = 0$ to $t = \infty$ is unity. The area under the curve between any two times, t_1 and t_2, represents the fraction of the atoms with retention times between t_1 and t_2. Using Equation (XIII-18) it can be shown that the fraction of particles retained in the reactor for a period less than the mean retention time, Θ, is $(1 - 1/e)$ or 0.63.

When mixing predominates over direct displacement as the characteristic of flow through a piece of equipment, the above analysis shows that a substantial part of the feed material is retained for a very short time while another substantial part is retained for times much longer than the mean retention time. Accordingly if a definite time of retention is required to complete a chemical reaction, some substances may pass through unreacted while others are retained longer than necessary. One solution for this problem is to design the process as a

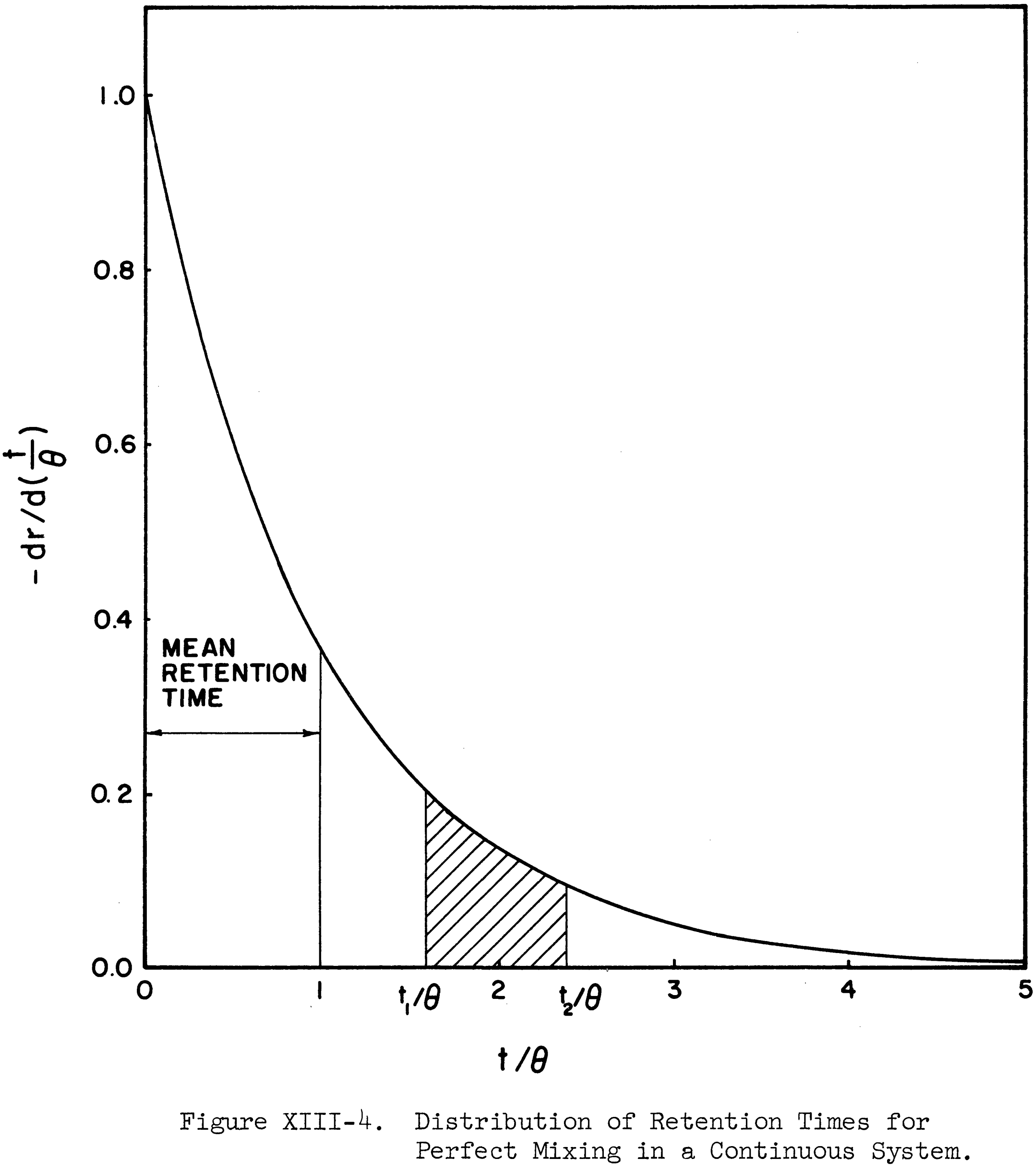

Figure XIII-4. Distribution of Retention Times for Perfect Mixing in a Continuous System.

multi-stage reactor. Another manner in which this difficulty may be overcome is through the use of a recycling stream. In the case of iron ores, a very effective method is to use magnetic separation of the completely reduced iron in the product stream of the reactor and to recycle the nonmagnetic material. Separation processes may be used in a similar manner depending upon the physical and chemical differences which exist between the product which is completely reacted and that which is only partially reacted.

Energy Balances

From the viewpoint of thermal equilibrium, a fluidized bed qualifies quite well as an ideal stage, since gases and solids entering such a bed attain bed temperatures almost instantaneously. Temperatures are essentially constant throughout a fluidized bed and the solid and gas streams are consequently at the same temperature. This is essentially true even when the gas and solid streams entering the bed are at temperatures very different from the bed, and also in cases where chemical reactions are occurring which involve large heat effects. On this basis, a heat balance may be written about each stage of a fluidized bed reactor. As in any other heat balance, the terms to be considered are the sensible heats of the reactants and the products, the heat evolved by any reactions taking place in the process, the heat losses and any additional energy supplied to the process. A carefully drawn heat balance should permit the operator of the equipment to carry out the process very close to the optimum temperature. In practice, the temperature of the process can be controlled by the adjustment of energy put into or taken out of the equipment itself or by control of the degree of preheating of the inlet materials.

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CHAPTER XIV

REVERBERATORY FURNACE SMELTING

The reverberatory furnace is often employed for extracting metals from their ores. Ore and fluxing agents are charged to a furnace to which external heat is supplied, bringing about melting and at the same time chemical changes necessary to produce the metal (or sometimes matte) from compounds existing in the ore. A reducing agent, often in the form of powered coal such as used in tin smelting, is added. The charge materials are essentially those added to the blast furnace, but when the operation is carried out in a batch process, the term used to describe it is simple smelting.

Reverberatory furnace smelting is a key step in the extraction of copper from its ores. Ore and liquid slag from the converting step containing copper, iron, sulfur and oxygen along with gangue oxides such as silica, alumina, magnesia, etc. are charged to the furnace. This mixture is heated to temperatures above 1200°C so that the entire charge is molten. Two liquid phases result: (1) a copper matte consisting of copper, iron and sulfur, and (2) a slag which is a solution of iron oxide, silica, alumina, magnesia and other oxides but with a low copper content. These two phases separate under the influence of gravity, the heavier matte accumulating in the bottom of the furnace. These two liquids are tapped from the furnace, and are the principal products of the process. In addition, some reactions yield sulfur dioxide and other gases from the burning of the fuel which pass out through the flue. The essential features of a reverberatory furnace for carrying out this process are shown in Figure XIV-1.

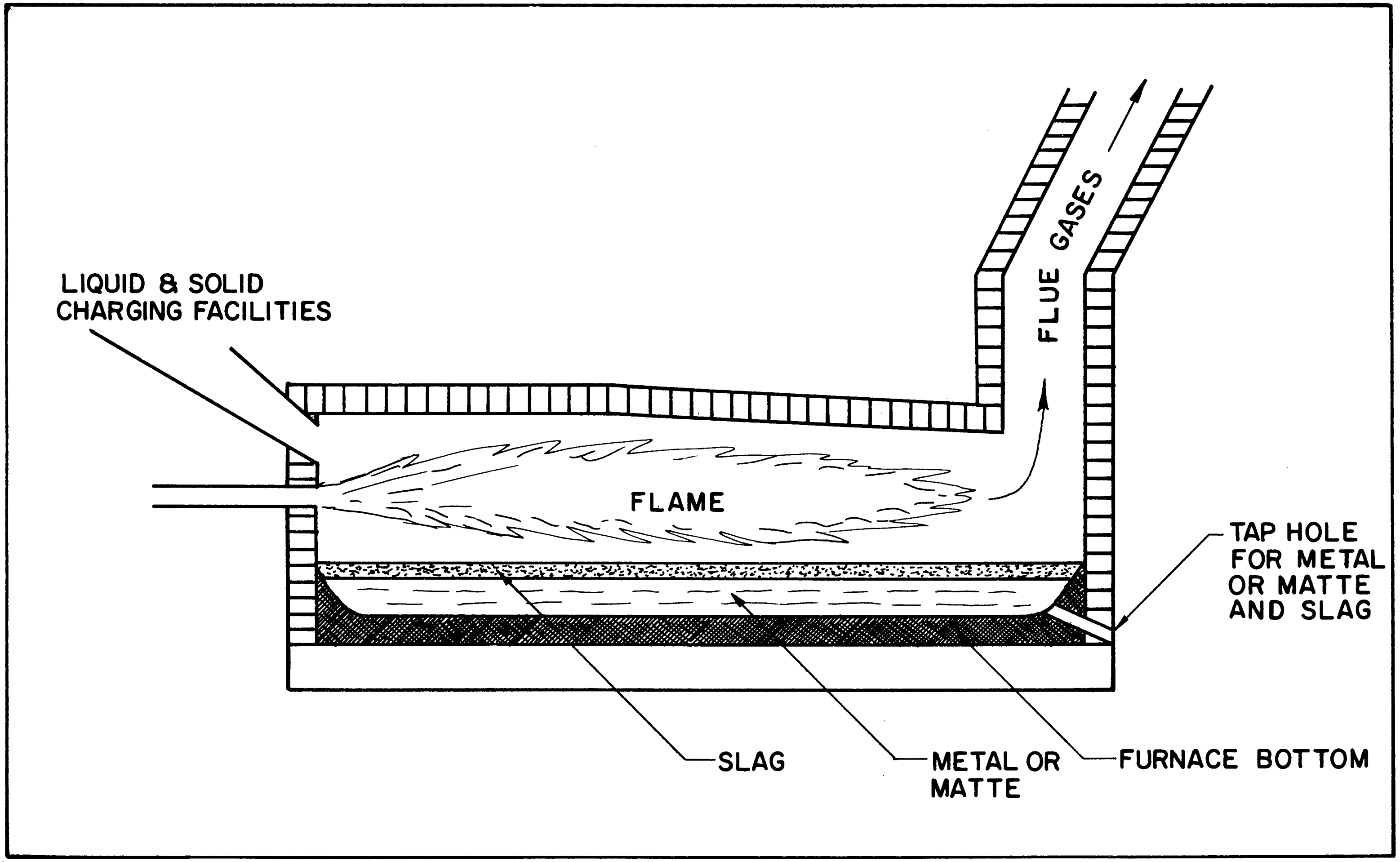

Figure XIV-1. Reverberatory Furnace Smelting.

For the successful operation of a smelting process, it is important that the engineer understand the operation and be able to express it in terms of mass and energy balances. A knowledge of the equilibrium relationships involved in the process and consideration of the rates of reactions involved will permit a mass balance to be written for the process. Similarly the energy balance and specification of the fuel requirements may be determined from the sensible heat of the input materials, the heats of reaction, and a knowledge of the heat losses from the process. These factors which affect the smelting operation in the reverberatory furnace are considered below, and for illustrative purposes are treated in terms of copper smelting operations.

Material Balance

A metallurgical balance for the copper reverberatory furnace has been prepared showing the variations in charge requirements for several matte grades.[1] The material balance often involves a number of assumptions, particularly regarding the products of combustion. The compositions of the charge materials are usually known, or may be assumed to be typical of the practice used. The products of the smelting operation may usually be assumed to be in equilibrium with respect to distribution of elements between slag and matte or metal, or to be typical of the smelting practice involved.

On this basis and making the use of element balances, a material balance may be made for the reverberatory furnace. Depending upon the desired composition of matte to be produced, one may compute a smelting charge requirement.[6]

Energy Balance

A list of the reactions involved in the fusion of the complex mixture which is charged to the reverberatory furnace in copper smelting would be extremely long. Any attempt to quantitatively relate the energies involved in that given list of reactions with what actually takes place in the reverberatory furnace is essentially impossible. The ore charged into a reverberatory furnace may contain Cu_2S, Cu_2O, CuO, $CuSO_4$, FeS, $FeSO_4$, Fe_2O_3, Fe_2O_3, and SiO_2, together with various complex silicates of iron, aluminum, etc. In addition, the complex mixture of converter slag which is recycled to the reverberatory furnace is also added along with silica and other components in the fluxing agents. On the basis of the assumptions used in making the material balance, one might make a reasonable guess at the heat evolved by reaction during reverberatory smelting. One difficulty over and above the complexity of the situation which exists in the furnace is the fact that data in general are lacking on the heats of solution and heats of reaction for most of the systems involved.

In view of this fact, an estimation of the energy requirements for reverberatory smelting might be made by neglecting energies of reaction for the system. The energy balance then becomes a summation of the sensible heats of the products minus the sensible heats of the reactants and the heat losses from the furnace. The figure resulting from the summation should be the fuel requirement. The sensible heat of the materials may be estimated from specific heats. Although specific heats may not be available for the actual materials involved, they can be estimated by consideration of the specific heats of the elements themselves in the quantities in which they are present or through the use of some overall mean specific heat representing a material which is typical of the total charge in the furnace.

The heat losses may be estimated by consideration of the rate of heat conduction through the construction materials of the furnace. This heat loss must be equal to that lost by radiation and convection from the outer surfaces of the furnace. Specific attention should be given to the heat losses from furnace openings during charging. In view of the extremely high temperature of the interior of the furnace, heat losses through furnace openings for relatively short periods of time represent a major fraction of the total heat loss of the unit.

Kinetics of Reverberatory Smelting

In view of the fact that relatively little is known about the particular equilibria which exist in the furnace, relatively little may be said about the rate controlling steps involved in the smelting process. In view of the fact, however, that the product of a smelting process is two liquid phases, a slag and a metal (or matte), the rate of approach to equilibrium, when equilibrium is known, may be estimated from either the rates of the chemical reaction which is involved or the rate of transport of a given species from one phase to the other. The principles involved in such a calculation are outlined in detail in Chapter XX.

Heat transfer in the open hearth steelmaking process has been reviewed by B. M. Larson.[12]

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CHAPTER XV

THE BLAST FURNACE

The blast furnace process consists of charging ore, fuel and flux into the top of a shaft furnace and blowing heated air or blast into the bottom. This process is the backbone of the steel industry, producing a high-carbon, high-silicon, high-manganese cast iron which is converted to steel in the steelmaking furnaces. The process is also used for the production of lead. In the case of the iron blast furnace, the approximate relations between the reactants and products is such that per ton of iron produced, approximately 2 tons of ore, 0.9 tons of coke, 0.4 tons of a mixture of limestone and dolomite, and 3.4 tons of air is charged into the furnace. From these materials there is produced 1.0 tons of iron, 0.6 tons of slag, 0.1 tons of flue dust, and 5.1 tons of blast furnace gas. This rough statement relates to the production of pig iron in Northcentral United States, about 75% of the production in the U.S.A.

Iron is supplied to the furnace by ore in the form of the oxide, either hematite (Fe_2O_3) or magnatite (Fe_3O_4). Pure hematite contains 70% iron, but the present ore being mined from the Lake Superior region contains about 50% iron, the difference being represented by gangue, which consists mostly of silica and alumina, and about 12% moisture. Iron is also supplied by charging mill scale, sinter, slag from open hearth furnaces or Bessemer converters, and scrap. The fuel to provide temperature and also the source of the reducing agent is coke, the solid product of the destructive distillation of coal. Limestone and dolomite are added to form a fluid slag and to restrict the amounts of silica, sulphur and phosphorus entering the pig iron. The blast, which is heated air, sometimes enriched with oxygen, supplies oxygen to the process which reacts with the carbon of the coke to form carbon monoxide, the gaseous reducing agent. (Figure XV-1).

The blast furnace plant consists of several components, the principal one being the blast furnace structure itself. The blast is compressed by blowers and passes through stoves, where it is heated to a temperature of about 1550°F. The stoves involve regenerative heat transfer and fuel is supplied by the blast furnace stack gases, which have been treated to remove dust. In addition, the blast furnace operation requires charging equipment and ladles for the removal and transport of metal and slag. Secondary equipment includes a sinter plant where iron oxide from various steel-making operations, as well as from the dust collecting equipment of the blast furnace, and ore fines are sintered into a usable product. Coke ovens are necessary for the production of coke from coal, and often a fully integrated plant will also include production facilities for the manufacture of by-products from coke oven gases. A fully integrated steel plant will include in addition to these facilities complete steelmaking facilities and all the auxiliary equipment involved therewith. Discussion in this section will be confined to the iron blast furnace. It should be noted that the principles involved are the same in other blast furnace processes.

Chemistry of the Process

The principle reaction taking place in the blast furnace process is the reduction of iron oxide by carbon. The actual mechanism for this process involves gaseous reduction by carbon monoxide according to the reaction:

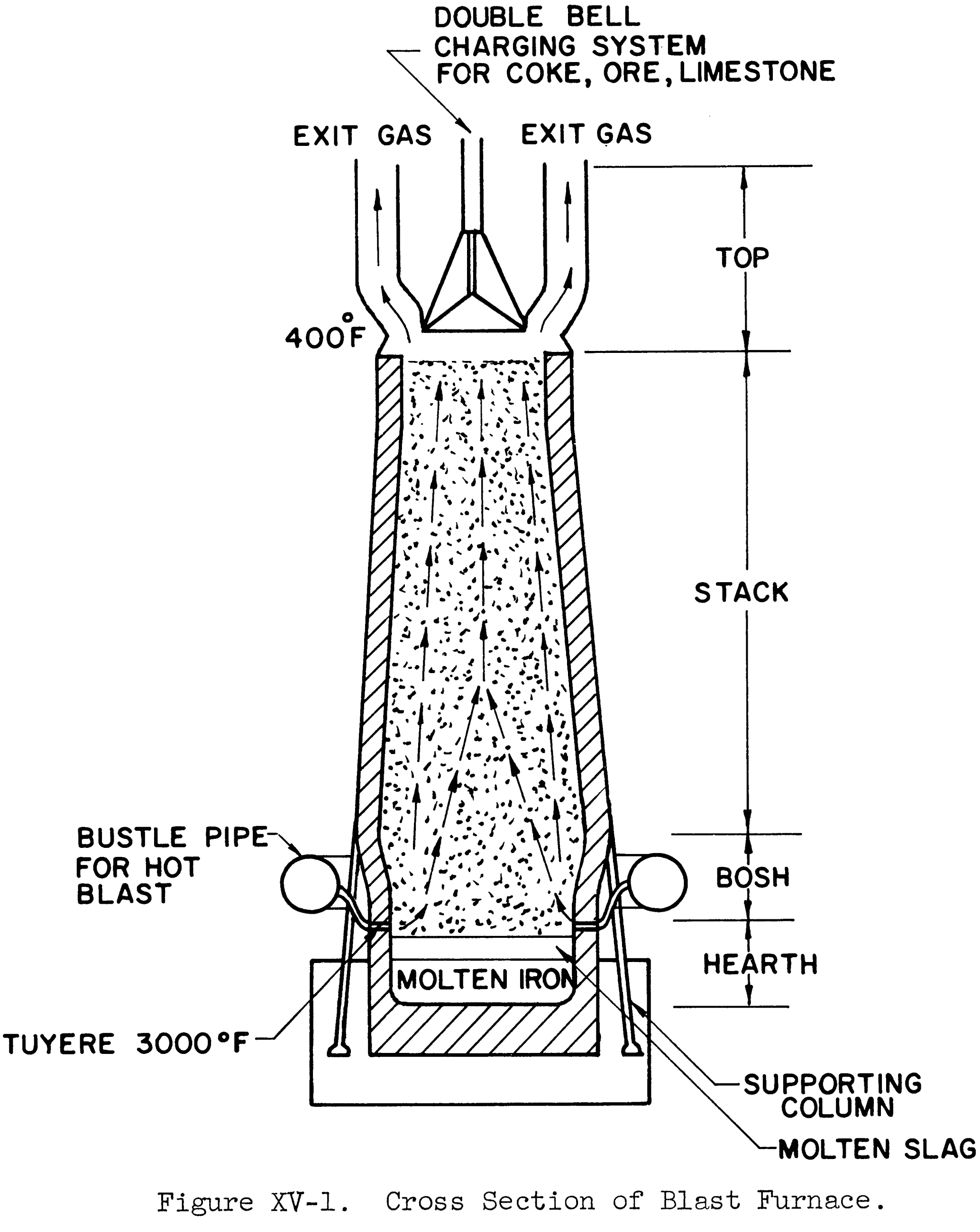

Figure XV-1. Cross Section of Blast Furnace.

$$3\ CO + Fe_2O_3 = 2\ Fe + 3CO_2 \qquad \text{XV-1}$$

In the presence of an excess of carbon at a high temperature, CO_2 is at once reduced to CO:

$$CO_2 + C = 2\ CO \qquad \text{XV-2}$$

The actual reduction of Fe_2O_3 by CO may take place in three steps, the Fe_2O_3 being successively reduced to Fe_3O_4, FeO and finally Fe. In addition to reducing the oxides of iron, carbon also reduces the oxides of manganese, silicon and phosphorous according to the reactions:

$$MnO + C = \underline{Mn} + CO \qquad \text{XV-3}$$

$$SiO_2 + 2\ C = \underline{Si} + 2\ CO \qquad \text{XV-4}$$

$$P_2O_5 + 5\ C = 2\ P + 5\ CO \qquad \text{XV-5}$$

The water vapor in the blast also plays a role in the process:

$$H_2O + C = CO + H_2 \qquad \text{XV-6}$$

The hydrogen liberated by the above reaction may react with iron oxide reducing it:

$$FeO + H_2 = H_2O + Fe \qquad \text{XV-7}$$

The water so formed is again decomposed. It should be noted that relatively few of the reactions involved furnish the heat required for the process, but that it is the oxidation of carbon and some of the reduction reactions involving carbon monoxide that furnish the heat to dry the raw materials, decompose the limestone, melt the iron and slag and to replace the heat losses.

Reactions (XV-3) through (-5) indicate that since the construction materials for the hearth are essentially pure carbon and the gas composition in the region of the tuyeres is controlled principally by the blast rate and temperature, and is not subject to great variation, that the distribution of the alloying elements, manganese, silicon, phosphorous and sulphur are controlled principally by the slag composition and temperature of the hearth. Between 50 and 75% of the total amount of manganese charged, principally in the ore, is found in the pig iron. The highest proportion being obtained with high hearth temperatures and basic slags. The amount of phosphorous in the iron is controlled directly by slag composition. A low temperature and a high basic slag are required to obtain low phosphorous. Sulphur which is carried into the furnace principally by the coke, and often by the ore, may be retained largely in the slag at high temperatures in the presence of carbon and a basic slag. The silicon content of the pig iron is controlled by the activity of silica in the slag. High temperatures and acid slags favor high silicon contents. In view of the extremely important role played by slag composition in the blast furnace process, considerable research effort has been expended on studies of blast furnace slags. The thermodynamic properties of blast furnace slags were recently reviewed by Chipman[3].

In addition to the role played by slag composition, the interaction of dissolved elements in liquid iron are also important with respect to blast furnace metal composition. The equilibrium constants for Equations (XV-3) through (XV-5) involve the activities of the dissolved constituents in the liquid metal. These activities are a function of the liquid metal composition, that is, the amounts of other alloying elements present. A principal interaction which occurs in blast furnace metal is that between carbon and silicon in solution. The solubility of carbon in liquid iron is greatly reduced by the presence of silicon as shown in Figure XV-2. Since the liquid pig iron leaving the blast furnace hearth is essentially saturated, i.e. at equilibrium with pure carbon at the temperature of the hearth, the activity of silica in the slag, which is a function of silica content, slag composition, and temperature, controls the silicon content of the metal which in turn controls the carbon content. The influence of temperature on the solubility of carbon in iron silicon alloys is also shown in Figure XV-2.

The relationships between activities of slag components and slag composition, and temperature, as well as the interactions which occur in the liquid metal are relatively well known. It follows that with this information, the heats of reaction and specific heats for the products and reactants when combined with the mass balance may be used to calculate an energy balance for the blast furnace process.

Blast Furnace Stoichiometry

A mass balance around the blast furnace not only describes in detail the mass flow of the streams going to and from the system and permits an energy balance to be written based on it, but is also very helpful in performing charge calculations. A material balance for the blast furnace requires a knowledge of the composition and amounts of each stream going to and from the blast furnace system. Often times this information is known with limited accuracy and one must therefore estimate or make assumptions concerning the disposition of given materials between various streams. The slag volume and theoretical slag composition may be calculated from lime, magnesia, silica and alumina

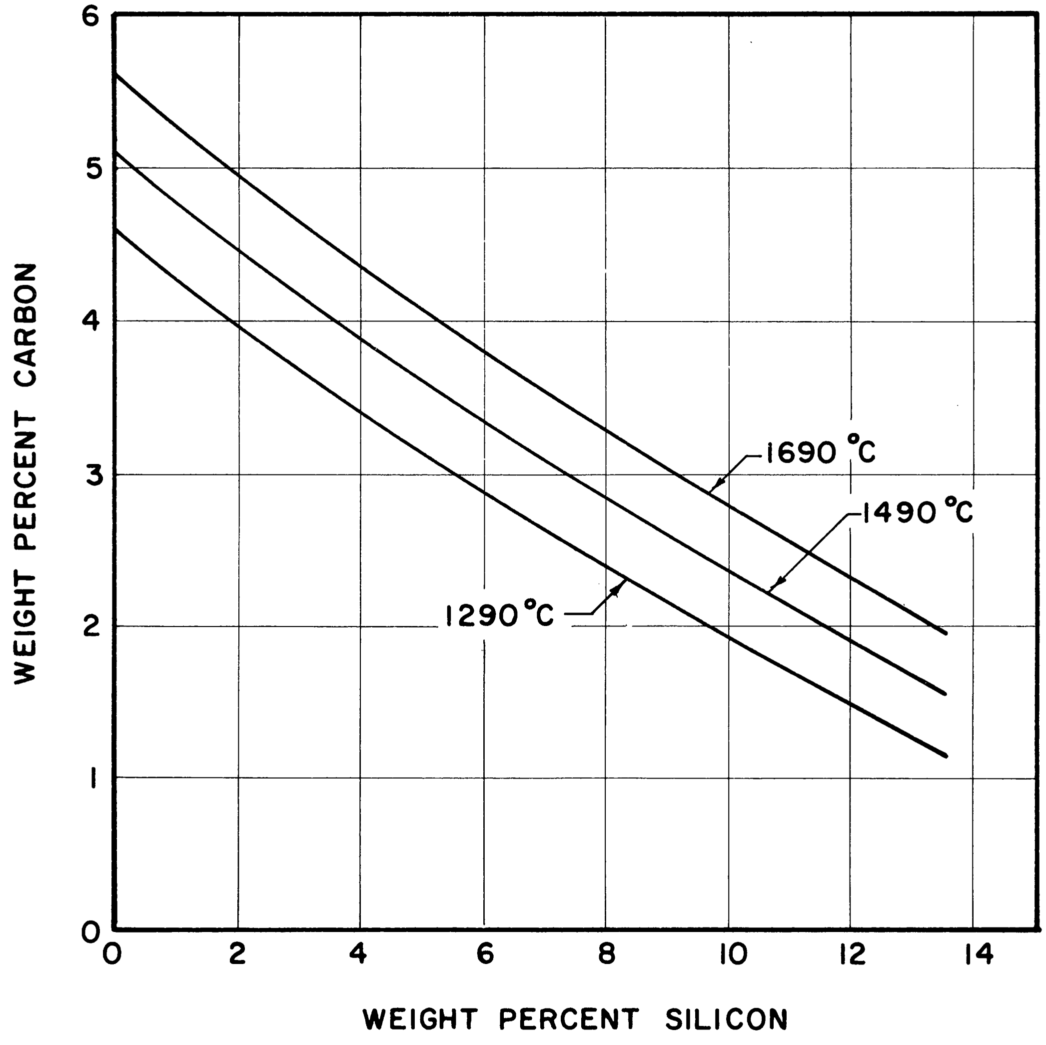

Figure XV-2. Solubility of Carbon in Iron-Silicon Alloys.

balances, an iron balance is used to calculate the mass of the metal stream, and carbon, oxygen and hydrogen balances are used to determine the exit gas volume and composition. Several examples of this type of calculation have been presented in the literature.[5,6]

Energy Balance

The total enthalpy balance for a blast furnace operation during a given reference period may be written in the form:

$$H_{\text{blast}} + H_{\text{burden}} + H_{\text{stone}} + H_{\text{coke}} = H_{\text{hot metal}} + H_{\text{slag}} + H_{\text{top gas}} + H_{\text{heat loss}} \qquad \text{XV-8}$$

It is necessary to solve the equation for the term, $H_{\text{heat loss}}$. In doing so, the sensible heat of the burden, stone and coke are taken as 0, since these components may be assumed to enter at 77°F, the base temperature. The sensible heats of the blast and hot metal may be computed directly. The sensible heat of the top gas may be computed using the reported CO-CO_2 ratio and assuming the ratio $H_2/H_2O = 4$. For normal operation, i.e., without high blast moisture or hydrocarbon injection at the tuyeres, the latter assumption has little or no effect on the over-all enthalpy balance. It is often necessary to assume a temperature for the exit gases. 400°F is often selected. In calculating the sensible heat of the slag, the stream is assumed to be a mixture of $2\ CaO.SiO_2$; $2\ CaO.Al_2O_3$; SiO_2; $CaO.SiO_2$; $2\ MgO.SiO_2$; and CaS.[7] Heats of formation[8] for these compounds and their specific heats[9,10] may be used to compute the sensible heat of the slag. It is a reasonable assumption to neglect the heats of mixing of these slag components and then whether the slag actually consists of the compounds or not is of no significance in the calculation. The heat loss term of Equation (XV-8) can now be computed.

Heat transfer in the blast furnace has been examined in some detail by Ceckler and Lander,[11] who concluded that furnace height should not influence the coke rate.

Thermochemical Model of the Blast Furnace

Recently a method of calculating the changes in blast furnace performance brought about by burden and/or blast modifications was developed.[7,12] The method is based on three simultaneous equations derived from the material and heat balances. These equations involve the computation of the moles of blast required to produce 1 pound atom of iron, the moles of carbon per pound atom of iron which act directly with oxides in the furnace, and the change in carbon rate per pound atom of iron as compared to the reference period carbon rate. The equations used to relate these three unknowns are a carbon balance an oxygen balance and an enthalpy balance. These three simultaneous equations are set up on the basis of the initial and final states of the various elements and their corresponding temperatures plus a furnace characteristic k defined by the equation:

$$k = H_{\text{heat loss}} / \text{mole of nitrogen per pound atom of iron for the given reference period.} \qquad \text{XV-9}$$

The thermochemical model is especially useful in problems connected with production planning. If an increase in the hot metal production is required from a group of blast furnaces, it is necessary to assess the costs involved and attain the desired production rate by various combinations of blast and/or burden modification. Performance data calculated using the model can provide information on which cost comparisons can be based. In view of the complexity and number of equations which are involved, this model is most conveniently handled by a digital computer as outlined in Chapter XXIV.

The variation in hot metal cost resulting from the use of various blends of available raw materials can be assessed using linear programming techniques. This approach was first used by Bailey[13] who incorporated into his linear program the statistical information developed by Flint.[14] A linear program involving the thermochemical model and in addition restrictions on the quality requirements for input and output streams and the economics of operating and freight costs can be used to optimize the blast furnace burden at different locations with regard to cost and production. Development of a thermochemical model and its use on the digital computer has resulted in the prediction of blast furnace performance with reference to the additions of water vapor, natural gas and oxygen in the blast.[15]

Blast Furnace Kinetics

The rate of production of hot metal from a blast furnace installation may be dependent upon many factors. It would appear, however, that the principal rate-limiting condition is fixed by the rate of supply of reactants and removal of products from the furnace. For given blast furnace dimensions, the rate is primarily limited by the supply blast, the maximum rate of blast being that which would be necessary to fluidize the blast furnace charge. This limit may be computed using the techniques outlined in Chapter XIII. For most blast furnace installations, the capacity of the blowing system is usually far below this limit, except for cases where the burden consists of extremely fine material. It has often been stated that in actual production facilities the real limiting factor which controls the blast furnace production is the ability of the material handling systems to supply reactants and remove products from the furnace. Successful integration of such auxiliary equipment as cranes, skip jack hoists, unloading and conveyor belt systems is discussed from the theoretical standpoint in Chapter XXV.

Numerous correlations have been drawn between furnace dimensions and daily production rates. The results of these correlations indicate that the rated daily production of a furnace is given by the hearth area in square feet multiplied by a factor which ranges from 2.0 to 2.6[1], the actual value depending upon the particular furnace burden. The daily production rate has also been related to the coke burned per day which is in turn determined by the area in square feet of an annular ring six feet wide in front of the tuyeres multiplied by the factor 6300. These relationships may also be used to indicate the proper number of tuyeres for a given hearth diameter. Such correlations are based on present practice and often serve as a guide to the design of blast furnace installations.

A further limitation on blast furnace production rate could be the kinetics of the reduction process. This has been discussed in some detail in Chapter XIII and will be considered only qualitatively here due to the mathetical problem of dealing with a strong temperature gradient throughout the furnace bed. One can, however, estimate the rate of reduction assuming that the process is carried out by pure carbon monoxide gas at the prevailing temperature of the furnace charge. Integration of this rate equation throughout the bed height would then give the required furnace height and the necessary residence time for the charged material.

Improvements in Blast Furnace Operation

In addition to design improvements, the principal advancements in blast furnace operation have been control of the blast humidity, oxygen enrichment of the blast, natural gas or other fuel enrichment of the blast, pressure operation and the increased use of beneficiated materials.

Over one-half of the material entering the blast furnace is air. Consequently, relatively small changes in humidity are important with regard to the amount of water carried into the furnace. The endothermic decomposition of the water vapor in the hot zone adjacent to the tuyeres absorbs considerable heat. This additional heat absorbed in the hearth of the furnace increases the amount of fuel required in the form of coke. Considerable fuel saving can be accomplished by drying the blast stream either by a refrigeration cycle or by passing the air through suitable drying columns.[15] This bears out the importance of the humidity of the blast with regard to blast furnace performance. Controlled humidity has been proposed as a means of regulating the blast furnace.[15]

Oxygen enrichment of the blast as a means of increasing furnace output has been proposed for some time. The availability of large supplies of low-cost oxygen as the result of advanced developments in steelmaking processes has made this proposal even more feasible. It has been predicted that a 6% oxygen enrichment of the blast would increase production rates from 20 to 25 per cent. The effect of oxygen enrichment is to decrease the nitrogen content of the blast. This should result in less heat being carried from the furnaces by the top gas, a decreased volume and velocity of the reacting gas with a corresponding reduction in flue dust production, and an increased rate of combustion of the coke with higher hearth temperatures.

The amount of oxygen passing through the furnace for a given gas velocity may be increased if the furnace is operated under pressure. Modifications to existing blast furnaces were made at the time of World War II and showed a 15% increase in production with a decrease in coke rate of about 12½% and in flue dust of about 33%. Top pressures approaching one atmosphere gauge have been obtained, although there is often considerable mechanical difficulty connected with the operation of a blast furnace under pressure.

Enrichment of the blast with natural gas has also been shown to result in a lower coke rate.

The beneficiation of materials improves burden properties by concentration and enrichment, and may also improve the physical form of the burden as well. The washing and sizing of the burden is a very important aspect in obtaining optimum furnace performance. Considerable economy is also obtained with regard to transportation of charge materials to the furnace site if they are beneficiated at the mine. In addition, sizing of material prevents channeling of the gases, with resulting efficiencies in mass and heat transfer in the furnace shaft, and also promotes a more uniform movement of the burden down through the furnace.

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CHAPTER XVI

Converting Processes

The term "converting" is used to denote a further operation in producing a metallic element from the output material of a smelting operation. Converting has come to be used almost exclusively in connection with processes which involve the further refining of primary smelted material by blowing an oxidizing gas through it. Strictly speaking, however, in the case of steelmaking operations, converting could also be applied to the open hearth and electric processes which involve the oxidation of primary smelted pig iron to steel. The operation is carried out for these two processes in a closed furnace and oxidation is provided by the addition of iron oxide. The discussion of this chapter, however, will be confined to converting operations in which an oxidizing gas is used.

The Bessemer Process

Sir Henry Bessemer of England patented the pneumatic converter process in 1856. Although the process has undergone several developments and considerable modification over the past century, it still maintains its essential features. Liquid pig iron, the product of the blast furnace, is charged to a vessel and air is blown through it, oxidizing the dissolved carbon, silicon and manganese to very low impurity levels. The product, which is essentially pure iron containing low levels of alloying elements, is termed steel. The operation of a Bessemer converter is presented schematically in Figure XVI-1.

In specifying the operating conditions for the Bessemer converter the engineer is interested in the oxygen requirements, i.e., the

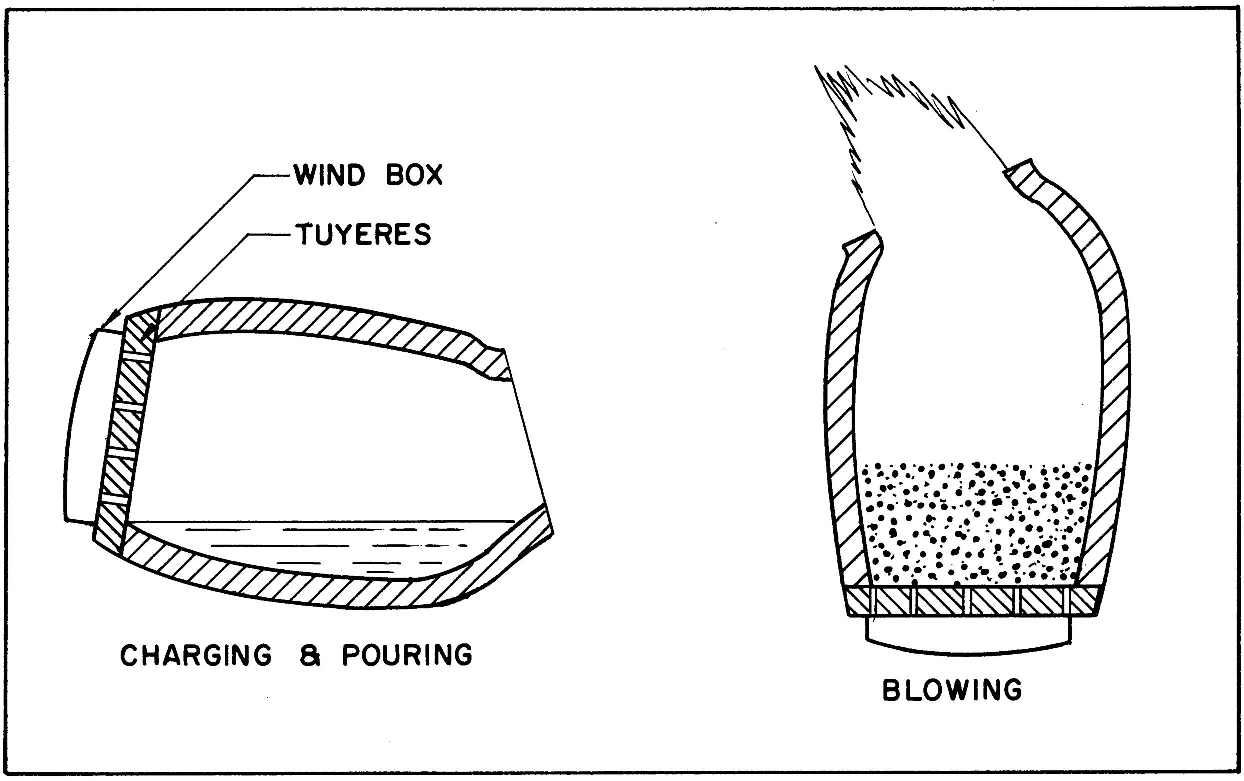

Figure XVI-1. Operating Positions of Bessemer Converter.

blast, the temperature of the metal, which determines the amount of scrap which may be added to the converter, and the time of operation. These operational features of the process may be specified by mass and energy balances and a consideration of the kinetics of the process.

Material Balance

The blast and flux requirements for the converting process may be determined from the initial and final compositions of the bath. Two items in the material balance which are particularly difficult to specify are: (1) The composition of the exit gases. Analyses of exhaust gases during the progress of a Bessemer blow indicated that early in the blow large amounts of carbon dioxide and some pure oxygen were evolved[1]. As the silicon content of the iron was reduced, however, the amount of CO in the exhaust gases increased. During the last two-thirds of a heat the exhaust gases then consisted essentially of carbon monoxide and nitrogen. Toward the end of the heat after the carbon had been removed, no composition data were reported. An assumption in this regard which is often made is that the blast is 100% effective and the exhaust gases contain carbon monoxide and carbon dioxide in the ratio of 4 to 1, as an average for the entire blowing period. (2) The loss of metal from the bath is difficult to specify. One often assumes that a fraction of the charged metal is lost from the mouth of the converter as iron oxide dust. This percentage varies with different practices but may be of the order of 2 or 3 %.

On the basis of typical hot metal charge analyses and typical end point steel analyses, a material balance may be written as outlined above. Similar material balances for copper converting have been presented[2].

Energy Balance

The energy balance for a converter is particularly important in determining the bath temperature. Since no external fuel is supplied, the process is completely autogenous. Consequently, an accurate specification of the amount of scrap to be added in order to prevent the converter from overheating is extremely important in converter operation.

The energy balance for a converter process may be written in terms of the sensible heat of the reactants and products, the heat generated by reactions during the process, and the heat losses. The sensible heat of the materials involved in the process may be determined by the data presented in Table XVI-1.

In order to specify the energies evolved by reactions taking place during the converter process, it is necessary to know the details of the chemistry of the blow.

The Bessemer blow may be roughly divided into three parts: the silicon blow, the carbon blow, and the after blow. This is illustrated in Figure XVI-2. The silicon blow begins immediately. The oxygen in the air units directly with the iron to form iron oxide which dissolves in the bath and combines with silicon and manganese. These reactions may be represented as:

$$2\,\mathrm{Fe} + \mathrm{O_2} = 2[\mathrm{FeO}] \tag{XVI-1}$$

$$2[\mathrm{FeO}] + \underline{\mathrm{Si}} = \mathrm{SiO_2} + 2\,\mathrm{Fe} \tag{XVI-2}$$

$$[\mathrm{FeO}] + \underline{\mathrm{Mn}} = \mathrm{MnO} + \mathrm{Fe} \tag{XVI-3}$$

The oxides of silicon and manganese form a slag with the excess iron oxide, evolving heat:

$$2\mathrm{FeO} + \mathrm{SiO_2} = 2\mathrm{FeO}\cdot\mathrm{SiO_2} \tag{XVI-4}$$

$$2\,\mathrm{MnO} + \mathrm{SiO_2} = 2\mathrm{MnO}\cdot\mathrm{SiO_2} \tag{XVI-5}$$

TABLE XVI-1

Sensible Heat Contents at Selected Temperatures Relative to a 77°F. Base Temperature[4]

Material	Temperature °F.	Heat Content BTU per Lb.
Preheated Steel Scrap	1250	172
Hot Metal, 1.00 % Silicon	2440	527
Hot Metal, 1.20 % Silicon	2500	540
Hot Metal, 1.40 % Silicon	2560	553
Blown Metal, Steel	2950	606
Basic Slag	3000	880

Gases	Temperature °F.	Heat Content BTU per Lb. Mole
CO	3000	23,200
CO_2	3000	37,400
CO_2	3500	44,700
N_2	3000	23,000
N_2	3500	27,300

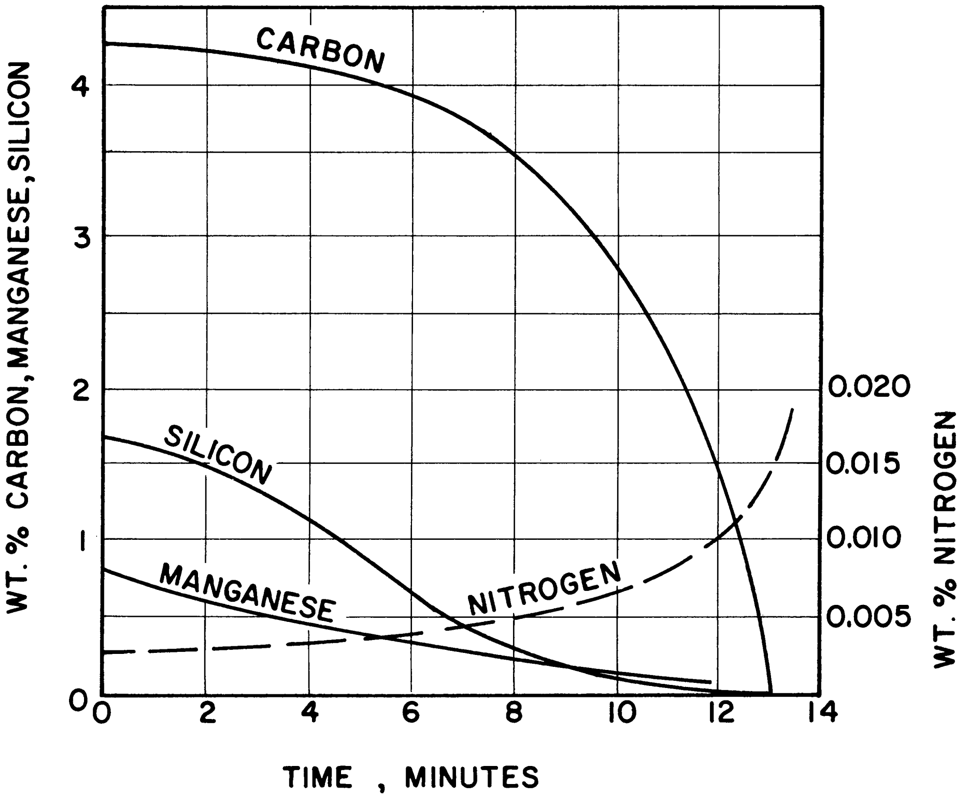

Figure XVI-2. Changes in Metal Bath Composition During Blowing Period of 25 Ton Bessemer Converter.

This particular phase of the blow lasts about five minutes during which the concentrations of silicon and manganese in the metal are markedly reduced. Toward the end of the silicon blow the carbon concentration begins to fall. Carbon may be oxidized either directly by the oxygen of the blast or by the dissolved oxygen in the metal. These reactions evolve heat and may be written as:

$$2\,\underline{C} + O_2 = CO \qquad \text{XVI-6}$$

$$\underline{C} + O_2 = CO_2 \qquad \text{XVI-7}$$

$$\underline{C} + \underline{O} = CO \qquad \text{XVI-8}$$

$$\underline{C} + 2\underline{O} = CO_2 \qquad \text{XVI-9}$$

These reactions account for the presence of both CO and CO_2 in the exhaust gases during the first phase of the silicon blow. At the beginning of the blow, carbon monoxide is subject to reduction by both silicon and manganese, especially if these elements are present in high concentrations. The reduction reactions may be expressed as:

$$2CO + \underline{Si} = 2\underline{C} + SiO_2 \qquad \text{XVI-10}$$

$$CO + \underline{Mn} = \underline{C} + MnO \qquad \text{XVI-11}$$

The temperature of the bath rises considerably during the silicon blow and this marks the onset of the second period or carbon blow. This period last six or seven minutes and the principal reactions occurring are represented by Equations (XVI-6, 7, 8, 9) and:

$$FeO + \underline{C} = Fe + CO \qquad \text{XVI-12}$$

$$2FeO + \underline{C} = 2Fe + CO_2 \qquad \text{XVI-13}$$

The two reactions above combined with Equation (XVI-8) may be used to account for the rapid final burnout of the remaining carbon. The remainder of the blowing period is referred to as the after blow.

On the basis of a mass balance and the heats of reaction, the heat evolved by oxidation of the metalloids from the bath can be computed. (Tables XXI-1, -2).

The principal source of error in writing an accurate heat balance for the converting process is in specifying the heat losses. An assumption which is often made is that the heat loss is equivalent to 20% of the heat evolved by the combustion of carbon to CO and CO_2. An experimental method has been suggested[2] for determining the heat losses by allowing the converter to stand for a short period and measuring the change of temperature with time. Such a technique would permit a reasonable estimate of the heat losses.

A heat balance for the oxygen converting process has been presented in detail, including consideration of blast rate and bath composition on the scrap which may be added to the process.[4]

One principal advantage which the open hearth process holds over the Bessemer converter is in its ability to handle a wide variation in types of charge. In order to generate more heat in the steel converter processes and thus utilize a higher fraction of scrap, ferrosilicon is often added to the converter, the oxidation of which supplies more heat units for the melting of scrap.[4]

The Oxygen Process

The availability of large quantities of oxygen has greatly altered the picture with regard to converting processes. Oxygen enrichment of the blast for the converting of copper mattes[5] or the use of pure oxygen in the LD process[6] for steel have received considerable development attention in recent years. The amount of available heat is increased greatly by removing the necessity of blowing nitrogen through the bath. Nitrogen behaves essentially as an inert except for some absorption toward the end of the blow in the Bessemer process. It does, however, remove considerable amounts of heat from the process which could have been used for the melting of scrap. Furthermore, the ability to supply larger quantities of oxygen to the process has increased the production rates thus reducing the cost per ton of material produced. The mass and energy balances for the oxygen process are essentially the same as outlined above for the Bessemer process except that the sensible heat carried away by nitrogen in the exit gases is now available for melting of scrap. Considerable expansion for the uses of oxygen in the basic metals industries is predicted[5,7].

Rate of Converting

The refining time required for the conversion of hot metal to steel in the Bessemer process is controlled by the rates of oxidation of the elements dissolved in the iron bath. These rates of reaction are controlled by the rates at which reactants arrive at the reaction site. It is possible that the process kinetics may also be controlled by the rate of the chemical reactions involved. However, in view of the high temperatures, it is most probable that the rate of the reaction is controlled by mass transport of the reacting species.

Several mechanisms for the oxidation processes involved in the converter operation are suggested by the equations above. Most of these reaction steps involve oxygen either in the gaseous or dissolved state. Consequently, a most likely rate limiting process is the transport of oxygen to the reaction site. Parlee, Seagle, and

Schuhmann[10] have studied the rate of the carbon-oxygen reaction in liquid iron. Based on their experiments, they concluded that oxygen transport is rate limiting. They expressed their results in the form:

$$\frac{dv_{CO}}{dt} = - \frac{D_O \; A}{\delta_{\underline{O}} \; V_M} \left(C_{\underline{O}} - C_{\underline{O}}^{\,t\,=\,\infty} \right) \frac{28}{16} \; \frac{1}{100} \qquad \text{XVI-14}$$

where dv_{CO}/dt is the rate of evolution of carbon monoxide gas in grams per second. D_O is the diffusion coefficient of oxygen in liquid iron which may be taken as $2\text{-}3 \times 10^{-4}$ cm^2/sec at temperatures near 1600°C. $\delta_{\underline{O}}$ is the boundary layer thickness. A is the area of the reaction interface, which in the case of the Bessemer converter may be taken to be the surface of the bubbles of gas passing through the melt. V_M is the volume of metal in cubic centimeters. $C_{\underline{O}}$ is the concentration of oxygen in weight percent. Similar expressions may be derived for reactions involving the oxidation of silicon and manganese. For these elements, however, one must consider in addition transport phenomena between slag and metal[11].

Larson[12] in considering the rate of the carbon reaction in the open hearth process showed that the rate of carbon removal was a direct function of the rate of boil. The rate of boil was shown to be a function of oxygen potential which Larson expressed as:

Rate of boil = (a constant) x (an oxygen potential $[\Delta O]$) x $(A/\Delta L)$.

The constant may include such things as a mobility or diffusion rate of some reactant in either a slag, metal, or gaseous phase. The driving force is a concentration gradient of oxygen across a phase boundary or diffusion film and the term $A/\Delta L$ is the ratio of an area such as slag-metal surface per unit weight of metal to the thickness of a transport or diffusion film. The interfacial areas and diffusion film thicknesses vary with turbulence in the system. It was concluded that a moderate increase in the potential or driving force term tending to deliver oxygen into the metal solution can greatly increase the boil rate. It was shown then that the minimum boil rate with oxygen supplied from air or combustion gases to a slag surface or through the metal as in the case of the Bessemer converter involves a series of many transport and reaction rate steps but is controlled essentially by a diffusion process of oxygen, CO_2, or H_2O through nitrogen (mainly) in a film zone of the order of a centimeter in thickness just above the bath surface.

The importance of supplying oxygen to the converting process on the overall rate is shown quite clearly by the fact that steel may be produced at a higher rate in the oxygen process than in the Bessemer process. Lack of highly precise data and the difficulty in determining the geometrical conditions which exist in a metal bath prevent a highly accurate picture to be drawn of the kinetics of converting processes. In specifying the operation of a converter with regard to time and blowing rate, one generally relies on previous experience. The techniques outlined in Chapter V for specifying the kinetics of a unit process are applicable here.

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CHAPTER XVII

ELECTROLYSIS OF FUSED SALTS

An important process for the production of reactive metals is the electrolysis of fused salts. Such processes are carried out at relatively high temperatures, and consequently, are quite distinct from electrolytic processes carried out in aqueous solutions. The principles involved are essentially the same, however. The engineering approaches to processes used for purification or the recovery of metals from leaching solutions are parallel to those which will be described under fused salt electrolysis in the present chapter.

In view of the fact that the chemically strong metals tend to react at high temperatures with most materials involving other metallic elements, a straightforward method for producing them is first to purify the salts of the reactive metals and then electrolize these salts for the recovery of the metallic element. This process is used for the production of aluminum, magnesium, beryllium, cerium, lithium, sodium, potassium, and calcium. It could also be used to produce less reactive materials, however, usually without economic advantage.

The electrolysis of a fused salt bath involves a container for the bath with some type of collection device available to handle the metal produced, and a cathode and an anode to supply the electric power for decomposition. A direct current is passed through the molten bath which may be the pure salt or the salt of a more reactive metal in which a compound involving the desired metallic element is dissolved. Examples of these two cases would be the production of sodium from pure liquid sodium chloride, or the production of aluminum, from a fused cryolyte bath (AlF_5-3NaF) in which a small amount of alumina is dissolved. If a fused salt bath contains several metallic elements which have similar decomposition potentials, a fractional decomposition of the bath is possible in which one may produce, first a pure metal, a, and then a pure metal, b, or in the event that the decomposition potentials are the same, an alloy of a and b may be produced.

Because of the high temperatures involved in these processes, it is often necessary to supply external heat. This depends on the nature of the bath. In the case of aluminum production, the electronic conductivity of the fused salt is such that sufficient resistance heating of the fused bath itself occurs to maintain the temperature of the process. In the case of the electrolysis of magnesium from a chloride bath, the electronic conductivity of the salt is quite low and consequently, external heat must be supplied. Thus, from the aspect of efficiency of the process, one is interested in having a bath in which the conductivity is purely ionic, but it is often an advantage to have a fused bath in which the conductivity is partially electronic in order that the process may be self sustaining and not require external heat for the maintenance of temperature. The Hall process for the production of aluminum is one such example. Since the conductivity of fused salts, in general, increases with increasing temperature, it may be desirable to select a higher operating temperature in order to take advantage of the heating effect of the electronic conductivity of the salt. A further advantage of operating the bath at a higher temperature is the fact that the decomposition potential will undoubtedly be lower. The advantages, of course, are offset by the fact that the heat losses increase markedly as bath temperature is increased, a consideration which may all but wipe out the advantages mentioned previously.

Process Calculations

The process design engineer is particularly interested in the amount of metal deposited by a given current. Faraday's laws of electrolysis apply, defining the maximum theoretical quantity which may be liberated by a given amount of current. Faraday's laws may be summarized in the statement: "The mass of a substance involved in reaction at the electrodes is directly proportional to the quantity of electricity passed through the solution and to the equivalent weight of the substance." The actual recovery of metal for a given current may be less than theoretically predicted if part of the electrolytic action of the current is expended in some other way. There are very few cases where the current efficiency is 100%. The loss of ionic transfer because of electronic conduction through the salt, the presence of gas overvoltages, the loss through other resistances in the circuit, such as those where contacts are made between bus bars, and the presence of some polarization in the bath can result in the deposition of less metal than that which is theoretically predicted. If the overall average efficiency of the process is known, however, one may predict the amount of metal deposited for a given current.

From Faraday's law;

$$W = \frac{M}{N} \frac{i\ t}{F} \qquad \text{(XVII-1)}$$

W = weight of metal deposited, in grams

M = atomic weight of metal deposited

N = valance of the metallic ion in the bath

i = current in amperes

t = time in seconds

F = Faraday's constant, 96,496 abs. coulombs/equivalent

Equation (XVII-1) gives the weight deposited at 100% efficiency. If the actual current efficiency of the process is known, the equation may be modified to the form:

$$W(\text{actual}) = W(\text{theoretical}) \times \text{efficiency} \qquad \text{(XVII-2)}$$

The considerations involved in predicting a current efficiency for a process are discussed in detail in the next chapter.

An important aspect of the process is the voltage required to carry out the electrolysis. This may be computed from the free energy of decomposition of the metallic compound involved. Consider the Hall cell for the production of aluminum. In the Hall process, virtually pure alumina is added to a bath of liquid cryolite containing some fluorspar (CaF_2). This molten bath is contained in a carbon lined vessel. The carbon lining serves as a cathode for the electrolysis. Carbon is also used for the anodes which are inserted into the bath from above. Although it is contended that the sodium and fluorine ions play an important role in the process, the overall effect may be summarized by the anode and cathode reactions. At the cathode, pure aluminum (99% +) is deposited as a liquid. At the anode, pure oxygen gas is liberated which immediately reacts with the carbon anode material giving off a mixture of carbon monoxide and carbon dioxide gases. These reactions may be summarized as:

$$2Al\ (l) + \frac{3}{2} O_2\ (g) = Al_2O_3\ (s) \qquad \text{(XVII-3)}$$

$$\Delta F^\circ = -401{,}400 + 77.0T \text{ cal/mole} \qquad \text{(XVII-4)}$$

$$C\ (gr) + 1/2\ O_2\ (g) = CO\ (g) \qquad \text{(XVII-5)}$$

$$\Delta F^\circ = -26{,}760 - 20.98T \text{ cal/mole} \qquad \text{(XVII-6)}$$

It may be shown that at a temperature of 1000°C the CO/CO_2 mixture in equilibrium with graphite is essentially pure CO. In calculating the theoretical minimum voltage at which aluminum will be deposited at the cathode in the Hall process, it may be assumed that the anode gas is essentially pure carbon monoxide and that the salt bath is saturated with alumina. Calculating the free energy of the sum of the reactions given in Equations (XVII-3) and (XVII-5):

$$Al_2O_3\ (s) + 3C\ (gr) = 2Al\ (l) + 3CO\ (g) \qquad \text{(XVII-7)}$$

$$\Delta F^\circ = 320{,}120 - 139.9T \text{ cal/mole} \qquad \text{(XVII-8)}$$

The decomposition potential, E, is related to the free energy of reaction by the relation:

$$\Delta F^\circ = -n\mathcal{F}E^\circ \qquad \text{(XVII-9)}$$

where ΔF° is the free energy of the decomposition reaction, n is the number of equivalents taking place in the decomposition reaction, $\mathcal{F}$ is Faraday's constant, 96,500 ampere seconds per gram equivalent or 23,060 cal per volt-gram equivalent, and E° is the reversible decomposition potential in volts. For the above case at 1,000°C the result is:

$$E^\circ = 1.06 \text{ volts} \qquad \text{(XVII-10)}$$

There is still considerable speculation about how much the reaction voltage of the aluminum cell is affected by the oxidation of the carbon anode. The problem concerns the influence of the energy of formation of the carbon monoxide and carbon dioxide formed at the anode. In actual practice, the operating voltages of the Hall cell are of the order of five or six volts.

The discrepancy between the theoretically predicted value given above, and that actually obtained is the result of factors which are discussed in detail in Chapter XVIII. The current efficiency of the cell, however, is of the order of 80% or better.

An additional quantity in which the process design engineer is interested is that of the power requirement. From Equation (XVII-1) and the example given above, it may be shown that the theoretical power requirement for the production of one pound of aluminum at 1,000°C is about 1.4 kw hours. In actual practice, however, the power requirement is about 8.7 kw hr/lb.

From a heat balance of the electrolytic process, and a knowledge of the electrical conductivity of the bath at the temperature of operation, one may predict the rate of energy input necessary to maintain that temperature. This heat requirement may be in the form of a determination of the required current density to maintain the operating temperature, or having selected the current density, it may be in the form of the burning of a given amount of fuel, within the cell vessel, itself.

In the case of magnesium, the metal is recovered by electrolizing the chloride in a steel pot which serves as a cathode. The anode is made up of carbon rods inserted in the bath and external heat is supplied by burning natural gas. The magnesium is recovered as a liquid. Since it is lighter than the bath, it floats on the salt and is protected from oxidation by a fluoride flux or molten sulphur.

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Part IV

REFINING OPERATIONS

CHAPTER XVIII

ELECTROLYTIC REFINING

The electrolysis of solutions containing metallic ions is often employed to refine metals or to recover them from the products of leaching operations. Solutions containing metallic ions are electrolized to precipitate out the element in metallic form. Because of the difference in electrode potentials set up by different metallic ions in solution, it is often possible by electrolytic means to separate several metallic elements from the same solution[1].

The principles involved in electrolytic refining are essentially the same as those which were outlined in the previous chapter dealing with the electrolysis of fused salts. The basic differences arise from the fact that the processes are carried out at different temperatures and that the electrolyte is a molten salt in one case and an aqueous solution in the other.

A form of electrolytic refining which is often used is that in which a partially refined anode is placed in an electrolyte, a current is passed through the solution and at the cathode is plated out a highly pure elemental form of the desired material. In this particular case, since the anode and cathode are essentially the pure element being refined, the reversible cell potential is zero. The actual cell potential, however, is greater than this, the result of factors which will be discussed later. The design engineer who is dealing with electrolytic processes is interested in the power and voltage requirements to plate out a given amount of material, and also in the size of the operation, that is the number of tanks, the volume of solution, number of cathodes and anodes which would be involved, etc. The relationships which will yield these are merely an extension of the basic engineering material presented in the previous chapter.

Cell Voltages:

The cell voltages are comprised of several components. These may be summarized as: (1) the IR drop to overcome the resistance of the electrolyte, bus bars, connections, etc. (2) the reversible cell potential, (3) the polarization or over-voltage. The total cell voltage is the sum of these three potentials.

Ohmic Resistance

From Ohm's Law, $E = IR$, the contribution of Ohmic resistance of the solution to the cell voltage may be computed. R, the resistance of the electrolyte in question, may be calculated from the equation:

$$R = r\frac{l}{s} \tag{XVIII-1}$$

where: l = the average length of the flow path
s = cross sectional area
r = the resistivity of the electrolyte

The resistivity, r, may be determined by direct experimental methods and this is the general technique used. Often, resistivities or conductivities, the inverse of the resistivities, are tabulated for different electrolytes. In the case, however, where the solution is a complex one, it is seldom accurate to use the weighted average of the conductivities. Furthermore, it is nearly always necessary to consider the temperature dependence of the resistivity. The length of path of current flow, l, may be taken as the distance between the electrodes in the cell. For simple geometries, s may be taken as the size of the electrodes.

If, however, the electrodes are of different sizes, the average value is often a reasonable approximation. If the plates are relatively far apart, s can be assumed to be the size of the cross section of the tank or cell, independent of the size of the plates.

Reversible Cell Potential

The reversible cell potential may be calculated from Equation XVII-9:

$$E = \frac{-\Delta F^{o}}{n\mathcal{F}} \qquad \text{XVIII-2}$$

Equation XVIII-2 is often approximated by substituting ΔH^{o} for ΔF^{o} when the heat of reaction is known, but the free energy is not. This approximation is often referred to as Thomson's rule. Equation XVIII-2 would then become:

$$E = \frac{-\Delta H^{o}}{n\mathcal{F}} + \frac{T\Delta S^{o}}{n\mathcal{F}} \qquad \text{XVIII-3}$$

and Thomson's Rule would ignore the second term of that equation. As an example, the reaction potential for the electrolysis of water where $n=2$ may be calculated from the heat of reaction $-\Delta H^{o} = 68,370$ calories giving $E^{o} = 1.48$ volts. The correct value, however, calculated from the free energy change, $-\Delta F^{o} = 56,484$ calories is $E^{o} = 1.225$ volts. The error resulting from the use of Thomson's Rule is a function of the temperature of operation of the cell and the entropy change for the reaction. The error resulting may range as high as a volt or more in the calculated value of the reversible cell potential. As indicated above, it is often necessary to use this approximation. One should, however, be aware of its limitations.

Polarization

In general, it is not possible to compute accurately the value of the polarization or over-voltage. In practice, it is usually estimated from experience or data on similar electrodes or cells, but may often be modified with reasonable accuracy by considering the factors which influence it.

The chief contribution to the polarization potential of the cell is that of over-voltages, usually caused by gases, which is related to the potential required for the evolution of gas on an electrode. It has been found that over-voltages are functions of current density given by the Tafel relationship:

$$\mu = \beta \log \frac{i}{i_o} \qquad \text{XVIII-4}$$

where i_o is the exchange current density and β is the Tafel slope. μ the over-voltage may be estimated from this relationship if the coefficient β is known for the particular cell and electrolyte involved. The hydrogen over-voltage on an electrode has been found to be lower at higher temperatures. This is believed to be related to the activation energy for the reaction at the surface. The rate of this particular reaction is given by the Arrhenius equation

$$\text{Rate} = Ae^{\frac{-\Delta F^*}{RT}} \qquad \text{XVIII-5}$$

If the over-voltage itself is related to the reaction at the surface, suitable experiments should specify the coefficients in the Arrhenius equation and permit a prediction of the influence of temperature on the rate of reaction at the surface. The over-voltage is also a function of the nature of the electrode. The hydrogen over-voltage is high for lead, mercury, zinc, and tin, metals which are poor catalysts for the reaction:

$$H_2 = 2H^+ + 2e^- \qquad \text{XVIII-6}$$

This over-voltage, however, is quite low for platinum, iron, and silver, metals which are good catalysts for the above reaction. The over-voltage is also a function of roughness of surface. A rough surface has a low over-voltage, presumably because of the ability of the surface to act as a nucleating agent for the formation and evolution of the gas. The hydrogen over-voltage is also influenced by impurities in the electrodes, and the over-voltage tends toward the over-voltage of those impurities which are present. The source of impurities may lie, not only in the electrodes themselves, but in traces of metals in the electrolyte which may plate out at the cathode. The hydrogen over-voltage is also influenced by the electrolyte. However, this effect is generally quite small.

Another important source of the polarization potential is caused by concentration polarization in the neighborhood of the electrode. This polarization potential arises from the fact that the concentration of ions in the neighborhood of the electrode may be different from those in the bulk of the electrolyte solution. The concentration of ion in the bulk phase may be measured directly and that which exists at the surface may often be estimated, permitting a calculation of the concentration polarization potential. The relationships by which this polarization potential may be computed are shown in the following manner.

Consider, for example, a cell of the type

$$Cu(a_{cu}=1)\ |\ Cu^{++}(a_1)\ |\ Cu^{++}(a_2)\ |\ Cu(a_{cu}=1) \qquad \text{XVIII-7}$$

consisting of two pure copper electrodes emersed in solutions of copper-containing electrolyte in which the activities of the copper ion are equal to a_1 and a_2. The electrode reaction on the left is:

$$Cu(pure) = Cu^{++}(a_1) + 2e^- \qquad \text{XVIII-8}$$

with E_8 given by:

$$E_8 = E^o_{cu} - \frac{RT}{2\mathcal{F}} \ln (a_1) \qquad \text{XVIII-9}$$

Again, for the reduction on the right hand side; we have:

$$Cu^{++} (a_2) + 2e^- = Cu(\text{pure}) \qquad \text{XVIII-10}$$

$$E_{10} = E^o_{cu} - \frac{RT}{2\mathcal{F}} \ln \left(\frac{1}{a_2}\right) \qquad \text{XVIII-11}$$

where $E^o_{Cu} = E^o_{Cu}$. We obtain, therefore, for the cell reaction:

$$Cu^{++} (a_1) = Cu^{++} (a_2) \qquad \text{XVIII-12}$$

and for the cell EMF:

$$E_8 + E_{10} = E_{12} = - \frac{RT}{n\mathcal{F}} \ln \left(\frac{a_1}{a_2}\right) \qquad \text{XVIII-13}$$

The equivalent of such a concentration cell may exist in an electrolytic processing operation if the solution near the anode becomes depleted in metallic ions or if there is a build-up of ions in the solution at the cathode. The case of depletion of ionic concentration at the anode is illustrated in Figure XVIII-1. The concentration difference between the bulk solution and the solution near the electrode creates a potential difference which must be overcome and acts to increase the total cell voltage.

From Equation (XVIII-13), it is evident that the EMF of this concentration cell arises from a transfer of copper ions from the solution where the activity is a_1 to the solution where the ionic activity is a_2. Furthermore, it is shown that this EMF depends only on the ratio of the activities of copper ion in solution and not on the absolute value of the copper ionic activity. In the final cell EMF,

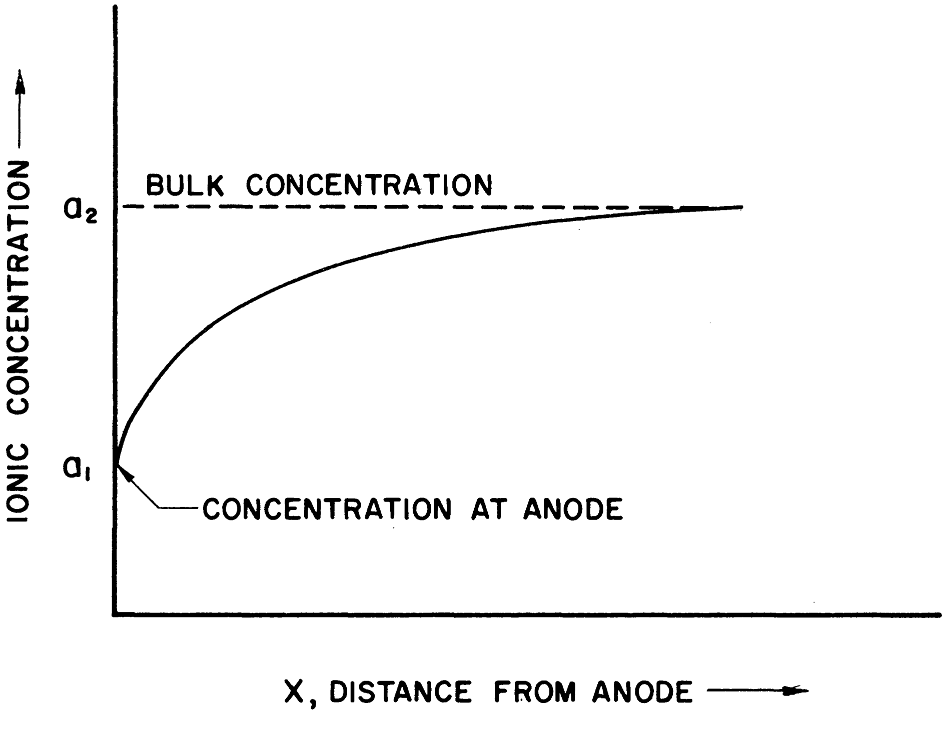


Figure XVIII-1. Concentration Polarization at Anode of Electrolytic Cell.

Equation (XVIII-13), E^o does not appear. This is true of all concentration cells. It may be concluded therefore, that for concentration cells, E^o is 0, and the EMF equation takes on the simplified form:

$$E = -\frac{RT}{n\mathcal{F}} \ln \left(\frac{a_1}{a_2}\right) \qquad \text{XVIII-14}$$

Since in cells of the type under discussion, a_2 and a_1 refer to the activities of the metallic ion in solution, we may assume that for dilute solutions, these are essentially equal to or are proportional in the same manner to the concentrations c_1 and c_2. Thus, Equation (XVIII-14) may be written approximately as:

$$E \simeq -\frac{RT}{n\mathcal{F}} \ln \left(\frac{c_1}{c_2}\right) \qquad \text{XVIII-15}$$

The equation in this form may be used to calculate the concentration polarization potential of a cell where c_2 refers to the surface concentration of the metallic ion in solution and c_1 refers to the bulk concentration. Since we are interested in the ratio of the two concentrations, any consistent units may be used to express it.

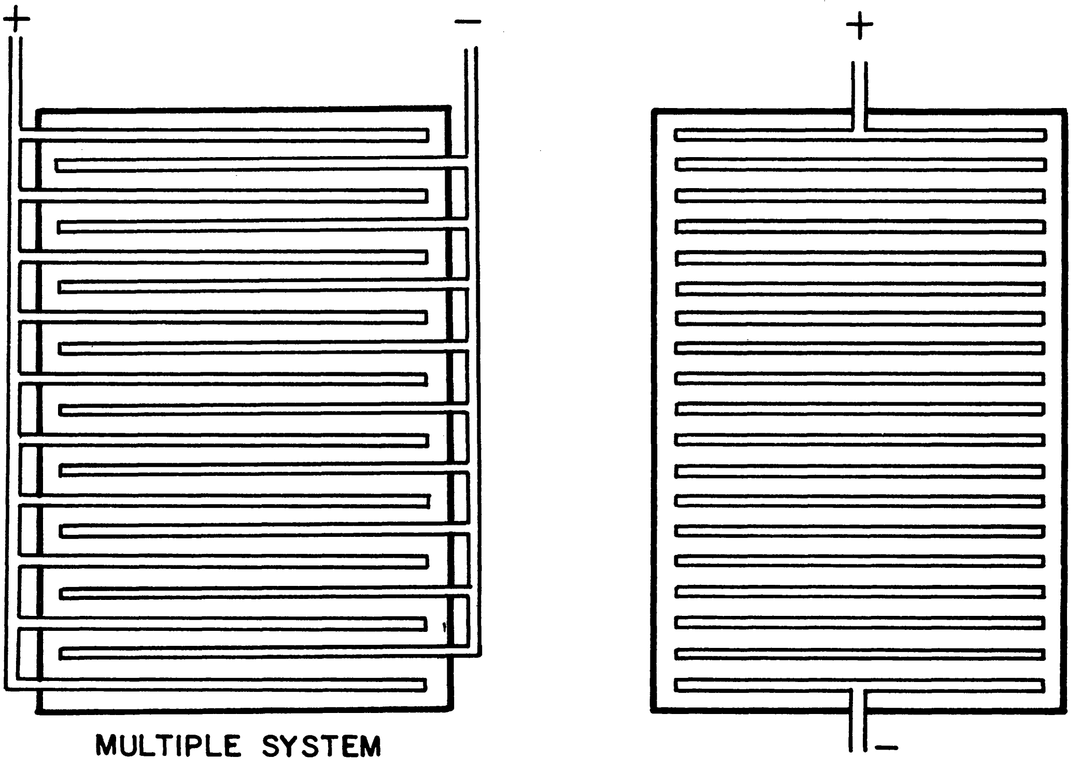
Film Resistance

A further contribution to the polarization potential is caused by the Ohmic resistance, i.e. the IR drop through the films at the electrode surface. Although the thickness of the film may only be estimated, the area is known and the current is known. The resistivity of the film is often difficult to evaluate, since there is a concentration gradient existing through it and the resistivity is a function of that concentration. The IR drops in the bus bars, the contact resistances and other Ohmic resistances which were included in the first term of the total cell potential are often lumped together with the IR drop through the surface films and the entire potential drop is often evaluated as the difference between that which is calculated and that which is actually measured in practice. It is therefore necessary that these contributions to the total cell potential be evaluated experimentally.

Computation of Total Voltage and Current

Several basic electrical systems are possible in electrolytic process equipment, depending upon how the connections are made. The two priciple systems, parallel and series, are shown in Figure XVIII-2. A parallel system is one in which the electrodes within each tank are connected in parallel so that the voltage drop across the entire tank is the same as that between any pair of plates in the tank. The advantage of this system is that there is a smaller voltage drop, consequently, fewer losses due to short circuits.

A series connection is one in which the plates within the tanks are connected in series. Consequently, the voltage drop across the cell is the sum of the voltage drops between each electrode. In the series system, each plate acts as an anode on one side and a cathode on the other, whereas in the parallel system, each electrode behaves as either a cathode or an anode, the reaction taking place on both surfaces. In general, less space is required. Also, there is no necessity for preparing special starting sheets for the series system. The tanks themselves, are usually connected in series, however, with the total number in the circuit being determined by the supply voltage and power of the generator. Although the pure series system is used in a few large refineries, the system which is most commonly employed in metallurgical



MULTIPLE SYSTEM
(PLATES IN PARALLEL)

SERIES SYSTEM
(PLATES IN SERIES)

Figure XVIII-2. Electrical Connections for Electrolytic Refining Cells.

plants is the multiple system in which the plates within each tank are connected in parallel, but the tanks themselves, are connected in series. The computation of the total voltage and current, then, for the plant, can be made using the principles of elementary electrical engineering.

Engineering relationships concerning the amount of metal theoretically deposited by a given current, the amount of current required to deposit a given amount of metal, and the reversible cell voltage requirements are presented in Chapter XVII. Details concerning the specific operation of electrolytic refining processes in the various metallurgical industries are presented in Reference 4. It should be noted in passing that electrolytic refining may also be carried out in a fused salt electrolyte.

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CHAPTER XIX

DISTILLATION PROCESSES

Distillation is the separation of the constituents of a liquid mixture by partial vaporization of the mixture and separate recovery of vapor and residue. Distillation processes conducted under vacuum are an important aspect of process metallurgical engineering. This process plays the principal role in the extractive metallurgy of zinc and mercury, and has been used to remove these volatile constituents from other metals, such as liquid lead. With the improvement in materials of construction and research advances, there is a growing interest in distillation processes for the refining of many metals including steels. The case of arsenic, for example, is of particular interest since there are many iron ores which contain arsenic and no suitable method has been developed to lower its content in the liquid iron produced. Fractional distillation has been shown to be a feasible method for the removal of this element from liquid iron.[1]

The engineering design of a vacuum distillation process requires that the vapor pressures of the constituents above the melt be known. Unfortunately, relatively few data are available on the vapor pressures of elements above liquid metallic solutions. However, the vapor pressures of pure elements are known with a relatively high degree accuracy, and the vapor pressures of a number of elements are presented in Table XIX-1.[2]

If the vapor pressure of the pure element is known, the partial pressure of that element above a metallic solution may be computed if the activity coefficient is known, using the relation:

$$P_a = P_a^o \ \gamma_a \ x_a \qquad \text{XIX-1}$$

TABLE XIX-I

VAPOR PRESSURE OF THE ELEMENTS*

Species	10^{-6} atm	10^{-5} atm	10^{-4} atm	10^{-3} atm	10^{-2} atm	1 atm
A						87.3(l)
Ag	1200(s)	1305	1442	1607	1816	2485
Al	1290(l)	1405	1545	1725	1940	2600
As_4	477(s)	517	563	622	708	895
At_2		270(s)	320	350	390	500
Au	1570(l)	1720	1896	2112	2388	3239
B	1500(s)	1600	1750	1900	2150	2800(l)
Ba	810(s)	890	985(l)	1116	1293	1911
Be	1390(s)	1505	1655(l)	1830	2070	2780
Bi	873(l)	960	1060	1190	1360	1900
Br_2	173(s)	186	203	222	245	331(l)
C	2720(s)	2920	3170	3450	3800	4775
Ca	790(s)	867	961	1075	1231(l)	1755
Cb	2820(l)	3050	3340	3700	4120	5400
Cd	485(s)	530	585(l)	657	744	1038
Cl	1450(l)	1550	1700	1850	2100	2800
Cl_2	114(s)	123	139	153	169	239(l)
Co	1750(s)	1900(l)	2100	2300	2600	3370
Cr	1350(s)	1465	1600	1755	1960	2495(l)
Cs	383(l)	425	476	544	634	963
Cu	1400(l)	1530	1685	1875	2117	2868
F_2					58(l)	85
Fr(87)			490(l)			950
Fe	1550(s)	1680	1837(l)	2033	2277	3008
Ga	1225(l)	1350	1500	1690	1920	2700
Ge	1370(l)	1500	1670	1880	2150	2980
H_2						20.39(l)
He						4.22(l)
Hf	2850(l)	3100	3350	3750	4150	5500
Hg	287(l)	316	351	394	449	634
I_2	241(s)	260	282	308	341	456(l)
In	1100(l)	1210	1350	1510	1730	2440
Ir	2580(s)	2800(l)	3040	3350	3700	4800
K	439(l)	475	534	605	702	1052
Kr						119.9(l)
La	1500(l)	1650	1800	2000	2250	3000
Li	705(l)	775	865	980	1130	1640
Mg	653(s)	715	789	881	1000(l)	1399

TABLE XIX-I
(cont'd)

Species	10^{-6} atm	10^{-5} atm	10^{-4} atm	10^{-3} atm	10^{-2} atm	1 atm
Mn	1140(s)	1240	1360	1570(l)	1750	2370
Mo	2530(s)	2740	3000(l)	3330	3750	5077
N_2						77.4(l)
Na	510(l)	558	623	705	813	1187
Ne						27.3(l)
Ni	1630(s)	1765(l)	1930	2130	2380	3110
O_2						90.2(l)
Os	2700(s)	2900	3160(l)	3470	3850	4900
P_4(yellow)	244(s)	268	296	334(l)	382	553
Pa	2250(l)	2450	2700	2950	3300	4500
Pb	887(l)	975	1088	1226	1408	2010
Pd	1660(s)	1800	2000(l)	2240	2530	3440
Po_2		660(s)	750	835(l)	945	1300
Pt	2160(l)	2340	2550	2820	3140	4100
Ra	650(s)	700	770	850	965	1410(l)
Rb	403(l)	445	496	561	650	952
Re	2900(s)	3150	3450(l)	3850	4300	5800
Rh	2200(s)	2400(l)	2600	2850	3200	4150
Rn						211(l)
Ru	2480(s)	2670	2900(l)	3180	3500	4500
S_2			500(l)			
Sb_2	860(s)	940(l)	1025	1160	1340	1890
Sc	1540(s)	1680(l)	1850	2050	2300	3000
Se_2	525(l)	568	620	679	755	1000
		(2 atm Se_6 and 10^{-4} atm Se at 1000°K)				
Si	1480(s)	1600	1740(l)	1920	2140	2750
Sn	1300(l)	1450	1600	1850	2150	3000
Sr	740(s)	810	900	1010	1150(l)	1657
Ta	3300(l)	3600	3900	4500	4800	6300
Tc(43)	2550(l)	2750	3000	3300	3700	5000
Te_2	655(s)	700	758(l)	825	907	1130
Th	2250(l)	2450	2700	2950	3300	4500
Ti	1640(s)	1800	1990	2210(l)	2500	3400
Tl	795(l)	870	965	1082	1235	1730
U	2000(l)	2150	2350	2580	2900	3800
V	1970(l)	2140	2340	2550	2900	3800
W	3230(s)	3490	3780(l)	4150	4625	5950
Xe						165.1(l)
Y	1750(s)	1900(l)	2100	2300	2700	3500
Zn	560(s)	610	672	750(l)	852	1180
Zr	2070(s)	2250	2450(l)	2700	3000	3850

* L. Brewer, Report for the Manhattan Project, MDDC-438C, 1946.

where P_a^o is the vapor pressure of pure component, a, at the temperature under consideration, γ_a is the activity coefficient of component a in the solution and x_a is the mole fraction. For dilute solutions, the activity coefficient of the solvent may be taken as one. If the solution is known to have ideal behavior, the activity coefficient of the solute is also one. Otherwise, specific experimental data are required to determine the activity coefficient of the solute. The vapor pressure of several alloying elements over dilute solutions in liquid iron at 1600° C are presented in Table XIX-2.

Clausius-Clapeyron Equation

From the combined statement of the first and second laws of thermodynamics, one may derive for a vapor-liquid equilibrium the relationship:

$$(S_v - S_l)\ dT = (V_v - V_l)\ dP \qquad \text{XIX-2}$$

or

$$\frac{dP}{dT} = \frac{\Delta S_v}{\Delta V_v} = \frac{\Delta H_v}{T\Delta V_v} \qquad \text{XIX-3}$$

This relation is known as the Clausius-Clapeyron equation. Its integration requires an experimental knowledge of ΔH_v and ΔV_v. If the volume of the liquid is small in comparison with that of the vapor, $\Delta V_v = V_v$ and if the vapor is ideal, $V_v = RT/p$, assumptions which are reasonable for metals at elevated temperatures. Substitution in Equation (XIX-3) gives

$$\frac{dP}{P} = \frac{\Delta H_v}{R} \frac{dT}{T^2} \qquad \text{XIX-4}$$

assuming that the right hand side of Equation (XIX-4) is constant; that is, ΔH_v, the enthalpy change accompanying the change from the

TABLE XIX - 2

VAPOR PRESSURE DATA FOR DILUTE LIQUID IRON SOLUTIONS AT 1600°C.

Element	Atomic Weight	Vapor Pressure Pure Element 1600°C-mm Hg	Activity Coefficient in dilute Solution γ^o	Vapor Pressure Over Dilute Iron Solutions 1600°C-mm Hg			Relative Volatility		
				0.05%	0.2%	1%	$\alpha_{Calc.}$	$\alpha'_{Calc.}$	$\alpha'_{Observed}$[1]
Al	26.94	1.9	0.031	0.00006	0.00024	0.0012	0.9	1.4	
Co	58.94	0.031	1	0.000015	0.00006	0.0003	0.5	0.5	
Cr	52.01	0.19	1	0.001	0.004	0.020	3.2	3.3	
Cu	63.54	1.0	8	0.0035	0.014	0.070	134.	125.	60.
Fe	55.85	0.060	1	- - -	- - -	- - -	1.	1.	
Mn	54.94	42.	1.3	0.028	0.11	0.55	900.	900.	150.
Ni	58.71	0.043	1	0.00002	0.00008	0.00041	0.7	0.7	
Pb	207.21	340.	1	0.046	(two liquids)		5700.	3000	
Si	28.09	0.42	0.0072	0.000003	0.000012	0.00006	0.05	0.07	(10)
Sn	118.70	0.8	1	0.00019	0.00076	0.0038	13.3	9.1	18.

liquid to the vapor state at equilibrium is essentially equal to that accompanying a change from one standard state to the other ΔH°_{V}, the equation integrates to the familiar form:

$$\ln \frac{P_2}{P_1} = -\frac{\Delta H_V}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \text{XIX-5}$$

This relationship may be used to extrapolate the data of Table XIX-1 to any desired temperature.

Equation (XIX-4) may be integrated to the general form:

$$\log P = \frac{-A}{T} + B \qquad \text{XIX-6}$$

where A and B are constants whose values depend upon the units in which the vapor pressure, P, and the absolute temperature, T, are expressed. This relationship permits the vapor pressures of materials to be tabulated in the form of two constants. Such tabulations are available in several sources.[3,4]

Relative Volatility

The term volatility is used to compare the vapor pressure of one pure substance with another. However, the vapor pressure alone does not define the ease of separation of the components from liquid mixtures, since the vapor pressure is a function of the presence of the other components. The partial pressure ratio of two components over a liquid solution is given by the relationship:

$$\text{Partial Pressure Ratio} = \frac{\gamma_a x_a P^{\circ}_a}{\gamma_b x_b P^{\circ}_b} \qquad \text{XIX-7}$$

The criterion for a successful distillation is that the molar (or mass) ratio of a component to be separated must be greater in the vapor phase than in the liquid phase. The coefficient of the molar ratio in solution in Equation (XIX-7) may be termed α where:

$$\alpha = \frac{\gamma_a P_a^{\circ}}{\gamma_b P_b^{\circ}} \qquad \text{XIX-8}$$

The relative volatility, α, is a direct measure of the ease of separation of components by a distillation process. Substances that are readily separated show large values of α. If α is unity, no separation is possible since the concentration of the two components in the vapor will be the same as in the liquid solution.

The relative volatilities of elements in liquid iron solutions[1] are included in Table XIX-2. The computed values of α indicate that lead, manganese, copper, tin and chromium may be removed from liquid iron; but that it would be impossible to remove silicon, nickel or cobalt from liquid iron, that is, that the relative volatility of iron is greater than that of the alloying element in these solutions. The calculations also indicate that aluminum has a relative volatility of one and would not be separated.

The relative volatility of two components changes with temperature. Viewed from the standpoint of ease of separation alone, the optimum temperature range in which to conduct the distillation is that in which the value of α is maximum. Equation (XIX-7) may be used to derive the following relationship between the concentration of the volatile component in the vapor phase, y_a, and in the liquid phase, x_a:

$$y_a = \frac{\alpha x_a}{1 + x_a (\alpha - 1)} \qquad \text{XIX-9}$$

Figure XIX-1 shows a plot of y versus x for various constant values of α.[4]

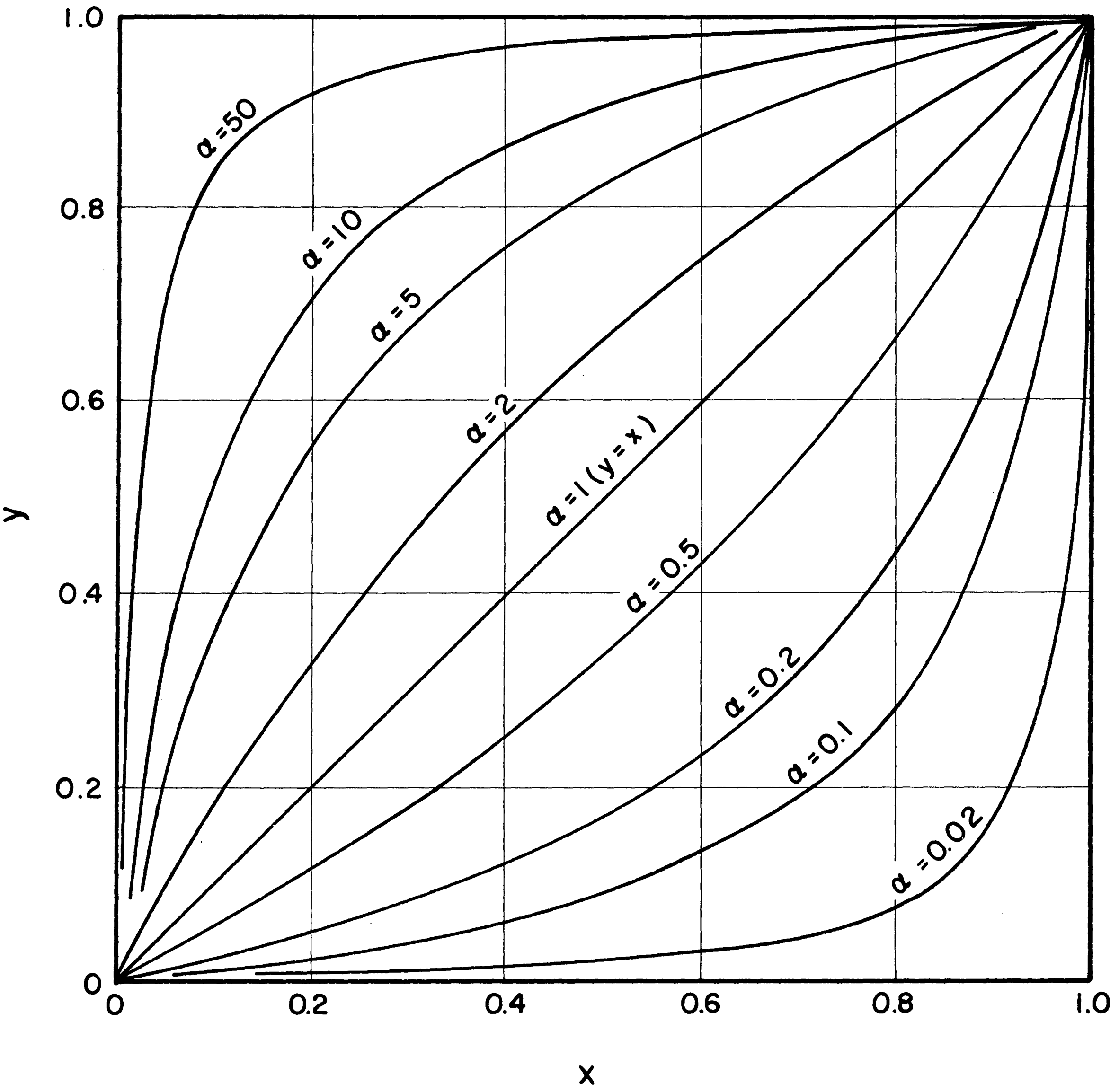

Figure XIX-1. Relationship Between X and Y for Various Values of α.

Equilibrium Distillation

The principal method of distillation used in metallurgical processes is simple batch distillation. In this process increments of vapor are removed upon their formation from contact with the residual batch of liquid solution. If the operation is not conducted under high vacuum conditions and one may presume that the vapor coming off the solution is in equilibrium with the bulk liquid, the following mathematical analysis may be applied.

The mass balance of such a process may be written in terms of a differential equation as was first done by Rayleigh.[5] The Rayleigh equation may be derived as follows: Assume a solution of two components, a and b, the total moles of which are L. Let the mole fraction of the more volatile component in the liquid be x, and the mole fraction of the same component in the vapor be y. Let dL moles be vaporized. The liquid will lose and the vapor will gain a differential quantity of the more volatile component. By a material balance,

$$(L - dL)\ (x - dx) + (y + dy)dL = Lx \qquad \text{XIX-10}$$

Neglecting differentials of a second order and rearranging,

$$\frac{dL}{L} = \frac{dx}{y-x} \qquad \text{XIX-11}$$

Integrating Equation (XIX-11) between limits,

$$\ln \frac{L_1}{L_2} = \int_{x_2}^{x_1} \frac{dx}{y-x} \qquad \text{XIX-12}$$

where L_1 = moles of original charge, L_2 = the moles of residual charge after $L_1 - L_2$ have been distilled off, x_1 = the mole fraction of more volatile component in the original charge L_1, x_2 = mole fraction of more volatile component in the residual charge L_2. Consistent weight units may be substituted for the molar units in Equation (XIX-12).

If experimental data giving the relationship between y and x are available, the right hand side of Equation (XIX-12) may be integrated graphically. If a mathematical relationship exists between y and x, the integration may be carried out analytically as in the following cases. During a simple batch distillation at constant pressure, the temperature rises as the residual liquid becomes poorer in the more volatile component. If α does not vary with temperature, Equation (XIX-9) may be substituted in Equation (XIX-12) with the integrated result:

$$\ln \frac{L_1}{L_2} = \frac{1}{\alpha-1} \left(\ln \frac{x_1}{x_2} + \alpha \ln \frac{1-x_2}{1-x_1} \right) \qquad \text{XIX-13}$$

If Henry's law applies to the solute which is being removed from the solution in the distillation process, the relationship $y=kx$ may be substituted with the result

$$\ln \frac{L_1}{L_2} = \frac{1}{k-1} \ln \frac{x_1}{x_2} \qquad \text{XIX-14}$$

It should be noted that Henry's law is also an isothermal relationship, and in order to assure validity of Equations (XIX-13 and XIX-14), one should be aware of any influences of temperature on the relationships involved.

One may also consider the application to multicomponent mixtures.[4] In the event that only one of the components of the complex solution is highly volatile, one may consider the solution as a pseudo binary. In the event, however, that two or more components have a volatility of the same order, one may compute the concentrations. The mathematics are more involved, but the principles are the same.

Molecular Distillation

In most metallurgical distillation operations, particularly those carried out under high vacuum conditions, the rate of distillation is such that it is controlled by the rate of evaporation of atoms from the surface of the melt, and one may not under these conditions presume that equilibrium is maintained between the concentrations in the vapor and in the liquid. A process conducted under these conditions is termed molecular distillation, and the quantitative rate of distillation under conditions of complete nonreturn condensation is given by the Langmuir Equation which may be derived as follows.

At any given temperature there is a maximum at which a volatile substance will evaporate from an exposed surface. This rate is very difficult to calculate from kinetic theory, but it can be estimated from the observed vapor pressure of the volatile substance. From kinetic theory, the rate of collision of molecules of vapor with the surface can be calculated from the pressure of the vapor. The mass of vapor molecules striking a square meter of surface per second, μ, is given by the relation,

$$\mu = \frac{\rho\bar{v}}{4} \qquad \text{XIX-15}$$

where ρ is the density of the vapor and $\bar{v}$ is the average molecular velocity. It may be shown, however, that

$$\bar{v} = 4\sqrt{\frac{R\,T}{2\pi M}} \qquad \text{XIX-16}$$

thus assuming the ideal gas law to hold:

$$\mu = P\sqrt{\frac{M}{2\pi RT}} \qquad \text{XIX-17}$$

where P = the pressure of the vapor and R is the gas constant, and M is the molecular weight of the vapor specie. In general, the number of molecules returning to the surface will be the same as the number striking it. At equilibrium, this will be the same as the maximum rate of evaporation. Therefore,

$$w_o = P_o\sqrt{\frac{M}{2\pi RT}} \qquad \text{XIX-18}$$

where w_o = the rate of evaporation in grams per square meter per second, P is equal to the saturation pressure in millimeters of mercury at the solution temperature, T is the absolute temperature in degrees Kelvin, M is the molecular weight.

Evaporation can occur at a rate of w_o only in a perfect vacuum, and when the rate of evaporation is so small that the mean free path of the vapor molecules exceeds the distance between the evaporating and condensing surfaces. At appreciable rates of evaporation, the vapor molecules will collide with each other. Some will rebound to the surface, so the actual rate of evaporation will be the difference between w_o and the rate of return to the surface w_1. The rate of that evaporation will then be:

$$w = w_o - w_1 \qquad \text{XIX-19}$$

The two rates w_o and w_1 are related to the pressures P_o and P_1. Therefore, the net rate of evaporation is given by

$$w = (P_o - P_1)\sqrt{\frac{M}{2\pi RT}} \qquad \text{XIX-20}$$

where P_1 is the partial pressure of the vapor at the evaporating surface.

The ratio between P_1 and P_o is the degree of saturation of the vapor, ϕ, it varies from 0 to 1 as the evaporating conditions vary from molecular to equilibrium evaporization. The degree of saturation is related in the following way to the relation between w, the observed, and w_o, the maximum, rates of evaporation.

$$\phi = \frac{P_1}{P_o} = 1 - \frac{w}{w_o} \qquad \text{XIX-21}$$

The actual rate of distillation is determined not so much by the rate of evaporation from the surface as by the rate of transfer of the vapor away from the surface. This rate of transfer is not as easy to calculate as the rate of evaporation. The factors which must be considered are:

1. pressure gradient of vapor
2. effective pressure of permanent gas in the system
3. dimensions of still and condensing system

Further discussion of these factors is presented in Reference 6.

Observations on Liquid Iron Alloys

Under conditions of molecular distillation, one must consider the influence of the molecular weight of the component on its rate of evaporation. If one does this, the relative volatility coefficient, α, Equation (XIX-8) may be modified to the form:

$$\alpha' = \frac{\gamma_A}{\gamma_{Fe}} \cdot \frac{P_A^o}{P_{Fe}^o} \cdot \sqrt{\frac{M_{Fe}}{M_A}} \qquad \text{XIX-22}$$

where M_{Fe} is the molecular weight of iron in the case under consideration, and M_A is the molecular weight of the solute. Under conditions of a dilute solution, iron obeys Raoult's law and γ_{Fe} is unity.

Also, the solute A at low concentrations obeys Henry's law, and γ_A is nearly constant and equal to γ_A^o. It would be equal to one if the solution were ideal. Under such conditions, α' becomes:

$$\alpha' = \gamma_A^o \cdot \frac{P_A^o}{P_{Fe}^o} \cdot \sqrt{\frac{55.85}{M_A}} \qquad \text{XIX-23}$$

A comparison is made in Table XIX-2 between the computed values of α' and those measured experimentally on liquid iron solutions.[1] Although there is some discrepancy, it should be noted that the comparative evaporation coefficients are in the same order as computed. The unusual results obtained for silicon and also for aluminum, where it was noted that in some cases aluminum was highly volatile and in other cases did not distill at all, are explained in terms of the formation of the highly volatile suboxides. This effect has also been noted by Floridis[7], who showed that the vacuum distillation of sulfur from liquid iron was greatly enhanced by the presence of silicon, presumably resulting in the formation of a volatile silicon sulfide, which assists in removing both elements from solution.

Recoveries by Condensation

Recovery of the distillate from distillation processes conducted as refining operations on liquid metals may be made by condensing the vapor to either the solid or liquid form. If a solid is formed, the efficiency of the recovery is essentially 100% provided that the solid condensate is in a form such that it may effectively be collected. In the case where the condensate is collected as a liquid, one may estimate the efficiency of the recovery from equilibrium conditions. The vapor pressure relations derived in Equations (XIX-6 and XIX-7) may be used to compute the partial pressures of the components over the condensed liquid. If it is assumed that the temperature of the gases leaving the condenser is the same as that of the condensed liquid and that equilibrium concentrations prevail, the fractions of vapor constituents escaping condensation may be readily computed from the partial pressures of components in the vapor phases entering the condenser and exiting from it.

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CHAPTER XX

LIQUID-LIQUID EXTRACTION

Liquid-liquid extraction is an operation which is often used in the chemical processing industries for removing one constituent of a liquid phase by equilibrating it with a second liquid phase which absorbs the desired constituent from it. The liquid phases must be essentially insoluble in each other, and it is desirable that the extracting phase have a higher solubility of the desired constituent, i.e., a lower activity coefficient.

The high temperatures at which most metallurgical operations are carried out presents an equipment problem in carrying out liquid-liquid extraction processes. Consequently, most extraction processes are carried out in batch operations, e.g., slag-metal or slag-matte equilibria are used for selective removal of constituents in steel and copper processing. The two-slag processes can be considered to be simple multiple-contact extraction processes. Thus, the mass and energy balances are straight-forward and directly obtained by consideration of the concentrations and weights of the phases involved.

The use of liquid-liquid extraction processes involving aqueous or organic solvents may also form a portion of an integrated metallurgical operation. The engineering approach is essentially the same as that outlined for other hydrometallurgical operations in Chapter IX. Equipment and mathematical treatments are described in several standard chemical engineering unit operation texts[1,2]. The focus of this chapter will be brought to bear on the equilibria and kinetics of high-temperature extraction processes.

Heterogeneous Equilibrium

Under equilibrium conditions, the free energy of each of the constituents is the same in all of the phases of a system. Thus, it can be shown that at constant temperature, the activity of a constituent in one phase bears a constant ratio to its activity in the other phase or phases. Consider, the distribution of iron-sulfide, FeS, between liquid iron and a slag. The constant activity ratio requires that:

$$\frac{a_{FeS(\text{in slag})}}{a_{FeS(\text{in metal})}} = \text{a constant} \qquad \text{XX-1}$$

If the activity in the slag phase is taken as the mole fraction, and that in the metal as the weight percentage, the ratio becomes:

$$\frac{N_{FeS(\text{in slag})}}{\%FeS(\text{in metal})} = L_{FeS} \qquad \text{XX-2}$$

Equation (XX-1) is an exact expression of the Nernst Distribution Law, and Equation (XX-2) represents an approximation to it based on the observed behavior of the phases involved, where L is the distribution coefficient.

The equilibrium constants of reactions in one phase of a two phase equilibrium may be related to those in the other by means of the distribution coefficients. At 1600°C. FeO distributes itself between liquid iron and a slag consisting of MnO and FeO in a constant ratio which may be expressed[3] as:

$$\frac{(FeO)}{(\% \underline{O})} = L_{FeO} = 4.4 \qquad \text{XX-3}$$

The constant of the reaction of manganese with FeO is given by:

$$\underline{Mn} + FeO(\text{in slag}) = \underline{Fe} + MnO(\text{in slag}) \qquad \text{XX-4}$$

$$K = \frac{(MnO)}{(\%\underline{Mn})(FeO)} = 2.3 \qquad \text{XX-5}$$

When Equations (XX-3 and XX-5) are combined, the equilibrium constant for manganese reacting with oxygen dissolved in the metal is found to be:

$$\underline{Mn} + \underline{O} = MnO(\text{in slag}) \qquad XX\text{-}6$$

$$K = \frac{(MnO)}{(\%\underline{Mn})(\%\underline{O})} = 10.1 \qquad XX\text{-}7$$

Kinetics of Liquid-Liquid Reactions

At the high temperatures involved in slag-metal or slag-matte processes, the rate of the exchange reaction is so great that equilibrium conditions may be assumed at the reaction interface, and the chemical reaction itself may be eliminated as a potential rate limiting step. The controlling mechanism then becomes a mass transport process in one of the phases present. The constituent which is present in the lowest concentration is usually the one with the slowest transport rate, since the driving force for transport is the smallest.

Darken[4] has considered the transfer reaction between manganese in steel and iron oxide in a contacting slag layer. The reaction is a straight-forward exchange reaction:

$$\underline{Mn} + Fe^{+2} = Mn^{+2} + \underline{Fe} \qquad XX\text{-}8$$

If the rate of one of the steps in the transport process is much lower than the others, then this step may be treated as the rate limiting one. In the process above, the concentration of iron in the metal is so high that its transport cannot be limiting. Generally, the concentration of manganese in the metal is much less than the concentrations of iron or manganese ions in the slag, so that the transport of manganese from the bulk metal to the reaction interface through a boundary layer in the metal may be assumed to be rate limiting. The process may be kinetically described as:

$$-\frac{d(C_{Mn})}{dt} = \frac{D_{Mn}\,A}{\delta_{mn}V}\left(C_{\underline{Mn}}(\text{bulk}) - C_{\underline{Mn}}(\text{boundary})\right) \qquad \text{XX-9}$$

The concentration of manganese at the boundary (slag-metal interface) is the concentration in equilibrium with the slag since mass transport in the metal is rate limiting. This concentration may be calculated from equilibrium relationships, considering the bulk concentrations of the other reactants to prevail at the interface.

Converting from molar concentrations to weight percentages, Equation (XX-9) becomes:

$$-\frac{d(\%\underline{Mn})}{dt} = \frac{D_{Mn}\,A}{\delta_{Mn}V}\left[\%\,\underline{Mn}\ (\text{bulk}) - \%\,\underline{Mn}\ (\text{equilibrium})\right] \qquad \text{XX-10}$$

which may be integrated to:

$$t = 2.3\,\frac{V}{A}\,\frac{\delta_{Mn}}{D_{Mn}}\,\log\left[\frac{\%\ Mn\ (t = 0) - \%\ Mn\ (\text{equilibrium})}{\%\ Mn\ (t) - \%\ Mn\ (\text{equilibrium})}\right] \qquad \text{XX-11}$$

Darken has estimated the practical result observed in open-hearth furnace operations using Equation (XX-11). Assuming that:

$\frac{V}{A}$, the bath depth is 34 cm.

δ_{Mn}, the boundary layer thickness is 0.003 cm.

D_{Mn}, the diffusion coefficient for manganese in liquid iron is 1.0×10^{-4} cm^2/sec.

The time required for a 90% approach to equilibrium, i.e., when log

$$\left[\frac{\%\underline{Mn} - \%\underline{Mn}(\text{equil})_{t=0}}{\%Mn - \%Mn(\text{equil})}\right] = 1,$$ is about 40 minutes.

This is in reasonable agreement with the observation that one half hour or more is required to reestablish manganese equilibrium after it has been disturbed by a major addition.

A similar analysis could be used to estimate the kinetics of other approaches to equilibrium, e.g., sulfur, chromium, etc.

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CHAPTER XXI

PRECIPITATION REACTIONS - DEOXIDATION

One of the principle methods of refining liquid metals is based on the insolubility of non-metallic compounds in liquid metals. The addition of materials to the liquid metal which result in the formation of an insoluble compound by reaction with an impurity element permits a refining separation to be carried out.

The calculation of addition requirements to effect a precipitation is based on the solubility product for the separating compound, or more precisely in terms of the equilibrium constant for the reaction involving its formation from solution by the dissolved reactants.

Equilibrium Constant for Deoxidation

In view of the fact that oxygen is almost a universal reactant in high temperature metallurgical process operations, equilibria between dissolved oxygen and other elements in the base material being refined are of prime importance in describing liquid metal processes. It should be noted that the formation of insoluble oxides may serve as a refining step in removing either oxygen or the metallic component of the oxide. In addition, the formation of a nitride, sulfide, carbide, or other insoluble compound is also a refining operation which may be described in the same manner.

The equilibrium between oxygen, a dissolved element, and the oxidation product which is usually a non-metallic "slag", or a gas in the case of carbon, hydrogen, or sulfur, may be expressed by the equation:

$$x\,\underline{M} + y\,\underline{O} = M_xO_y \qquad \text{XXI-1}$$

where $\underline{M}$ represents the element dissolved in the bulk metal, $\underline{O}$ is the dissolved oxygen which may be present as oxygen atoms or in combination with bulk metallic atoms (e.g., oxygen dissolved in liquid iron may be considered to be present as dissolved FeO), and M_xO_y is the oxide reaction product. The equilibrium constant for Equation (XXI-1) is:

$$K = \frac{a_{M_xO_y}}{a_{\underline{M}}^{x} \cdot a_{\underline{O}}^{y}} \qquad \text{XXI-2}$$

The influence of temperature is given by:

$$\Delta F^o = \Delta H^o - T\,\Delta S^o \qquad \text{XXI-3}$$

and,

$$\Delta F^o = -\,RT \ln K \qquad \text{XXI-4}$$

Experimental determinations of deoxidation constants involve not only the thermodynamics of the formation of the oxide product, but the formation of the solutions of oxygen and the reacting element in the bulk metal as well.

Aluminum Deoxidation of Steel

Consider the deoxidation of liquid steel by the addition of aluminum. The reaction is:

$$2\,\underline{Al} + 3\,\underline{O} = Al_2O_3 \qquad \text{XXI-5}$$

with equilibrium being specified by the constant:

$$K = \frac{a_{Al_2O_3}}{a_{\underline{Al}}^{2} \cdot a_{\underline{O}}^{3}} \qquad \text{XXI-6}$$

then: $$\log K = \frac{-\Delta H^\circ}{4.575\ T} + \frac{\Delta S^\circ}{4.575} \qquad \text{XXI-7}$$

I. FORMATION OF Al_2O_3 FROM PURE ELEMENTS

$$2Al(l) + 3/2\ O_2(g) = Al_2O_3\ (s) \qquad \text{XXI-8}$$

At high temperatures, i.e., near 1900°K., Elliott and Gleiser give:

$$\Delta F^\circ = -255,200$$

$$\Delta H^\circ = -401,400$$

$$\Delta S^\circ = (\Delta H^\circ - \Delta F^\circ)/T = -77.0$$

thus the free energy for Equation (XXI-8) is given by:

$$\Delta F^\circ_I = -401,400 + 77.0T \qquad \text{XXI-9}$$

II. SOLUTION OF ALUMINUM IN IRON

The activity of aluminum in liquid iron has been determined by combining the activity of aluminum in liquid silver with the results of measurements of the distribution of aluminum between liquid layers of silver and iron. The distribution measurements were reported by Floridis and Chipman[2] who computed a free energy of solution of aluminum in iron where the activity of aluminum is expressed in weight percent. The chemical equation and the thermodynamic relationship is given as:

$$Al\ (l) = \underline{Al}\ (\text{in liquid iron}) \qquad \text{XXI-10}$$

$$\Delta F^\circ_{II} = -12,900 - 7.70T \qquad \text{XXI-11}$$

III. SOLUTION OF OXYGEN IN LIQUID IRON

The equilibrium between H_2/H_2O gas mixtures and oxygen dissolved in liquid iron have also been measured by Floridis and Chipman[3]. The equilibrium may be expressed as:

$$H_2(g) + \underline{O} \text{ (in liquid iron)} = H_2O(g) \qquad \text{XXI-12}$$

where

$$K = \frac{P_{H_2O}}{P_{H_2} \cdot a_O} \qquad \text{XXI-13}$$

It was found that:

$$\Delta F^o = -32,200 + 14.63T \qquad \text{XXI-14}$$

However, the formation of water from the pure elements is given[1] as:

$$H_2 (g) + \tfrac{1}{2}O_2(g) = H_2O(g) \qquad \text{XXI-15}$$

and

$$\Delta F^o = -60,180 + 13.93T \qquad \text{XXI-16}$$

The difference between Equations (XXI-15 and XXI-12) gives:

$$\tfrac{1}{2}O_2(g) = \underline{O} \qquad \text{XXI-17}$$

with a free energy change:

$$\Delta F^o_{III} = -27,980 - 0.70T \qquad \text{XXI-18}$$

IV. COMBINING I, II, AND III

Combining:

$$Al_2O_3(s) = 2Al(l) + 3/2O_2(g) \qquad \text{(I)}$$

$$\Delta F^o_I = 401,400 - 77.0T$$

$$2Al(l) = 2\underline{Al}\text{(in liquid iron)} \qquad \text{(II)}$$

$$\Delta F^o_{II} = - 25,800 - 15.40T$$

$$3/2O_2(g) = 3\underline{O}\text{(in liquid iron)} \qquad \text{(III)}$$

$$\Delta F^o_{III} = -83,940 - 2.10T$$

one obtains the result:

$$Al_2O_3(s) = 2\underline{Al} + 3\underline{O}\text{(both in liquid iron)} \qquad \text{XXI-19}$$

$$\Delta F^o_{IV} = 291,660 - 94.50T \qquad \text{XXI-20}$$

or expressed in terms of the deoxidation constant:

$$\log K_{IV} = -63{,}700/T + 20.67 \qquad \text{XXI-21}$$

The deoxidation constant may then be calculated at any temperature in the steelmaking range, e.g. K_{IV} @ 1600°C = 4.7×10^{-14}

Summary of Deoxidation Data

A summary presentation of the free energies of formation of oxide compounds is given in Table XXI-1.[4,5] Also included are data for nitrides, sulfides, and carbides, compounds which may also be formed upon removal of an impurity.

In addition to the standard free energies of formation of the insoluble compounds, the standard free energies of formation of the solution containing the reactants is also required. Table XXI-2 presents the free energy relations for the formation of dilute solutions in liquid iron[4]. The data for other solvent metals is less complete, with only a few values being scattered throughout the literature.

In many cases, an estimation of the deoxidizing power of an element may be made by assuming that an ideal solution is formed between the element and the solvent metal (i.e., the mole fraction of the dissolved element may be substituted for its activity). If the free energy of formation of the solution between oxygen and the solvent metal is unknown, however, the equilibrium oxygen activity may only be specified in terms of an equivalent oxygen partial pressure in the gas phase. This information may be useful to the process engineer if the oxygen potential of the system is determined by other conditions which are known.

TABLE XXI-1

STANDARD FREE ENERGIES OF FORMATION OF OXIDES, SULFIDES NITRIDES AND CARBIDES AT 1600 °C

No.	Reaction	ΔH° Cal per mole	ΔS° Cal per mole per deg. K
	OXIDES		
1	$2Al(l) + 3/2\ O_2 = Al_2O_3\ (S)$	-401,400	-77.00
2	$Be(l) + 1/2\ O_2 = BeO\ (S)$	-142,360	-23.36
3	$C(graphite) + 1/2\ O_2 = CO(g)$	- 26,760	+20.98
4	$C(graphite) + O_2 = CO_2(g)$	- 94,260	+ 0.27
5	$Ca(g) + 1/2\ O_2 = CaO\ (S)$	-187,980	-46.21
6	$2Cb\ (S) + 5/2\ O_2 = Cb_2O_5\ (S)$	-417,770	-81.58
7	$Co(l) + 1/2\ O_2 = CoO(S)$	- 57,380	-18.65
8	$2Cr(S) + 3/2\ O_2 = Cr_2O_3\ (S)$	-271,300	-61.82
9	$Cu(l) + 1/2\ O_2 = CuO(l)$	- 33,110	-18.21
10	$Fe(l) + 1/2\ O_2 = FeO(l)$	- 57,070	-11.60
11	$H_2(g) + 1/2\ O_2 = H_2O\ (g)$	- 58,850	-13.12
12	$Mg(g) + 1/2\ O_2 = MgO(S)$	-176,060	-49.84
13	$Mn(l) + 1/2\ O_2 = MnO(S)$	- 97,360	-21.12
14	$Mo(S) + O_2 = MoO_2(S)$	-131,530	-33.95
15	$Ni(l) + 1/2\ O_2 = NiO(S)$	- 57,370	-22.09
16	$Si(l) + O_2 = SiO_2(S)$	-217,780	-46.91
17	$Sn(l) + O_2 = SnO_2(S)$	-138,500	-48.92
18	$2Ta(S) + 5/2\ O_2 = Ta_2O_5(S)$	-480,030	-96.65
19	$Ti(S) + O_2 = TiO_2(S)$	-224,080	-41.93
20	$2V(S) + 3/2\ O_2 = V_2O_3(S)$	-291,350	-56.49
21	$W(S) + O_2 = WO_2(S)$	-136,750	-40.93
22	$Zr(S) + O_2 = ZrO_2(S)$	-258,170	-42.87
	SULFIDES		
23	$2Al(l) + 3/2\ S_2(g) = Al_2S_3(S)$	-164,400	-69.0
24	$Ca(g) + 1/2\ S_2(g) = CaS(S)$	-169,600	-47.4
25	$2Cu(l) + 1/2\ S_2(g) = Cu_2S(l)$	- 29,300	- 6.2
26	$Fe(l) + 1/2\ S_2(g) = FeS(l)$	- 34,000	-10.4
27	$Mg(g) + 1/2\ S_2(g) = MgS(S)$	-132,300	-45.7
28	$Mn(l) + 1/2\ S_2(g) = MnS(S)$	- 68,700	-19.1
29	$Mo(S) + S_2(g) = MoS_2(S)$	- 76,300	-33.3
30	$Si(l) + S_2(g) = SiS_2(S)$	- 73,200	-44.0
31	$W(S) + S_2(g) = WS_2(S)$	- 69,800	-32.9

TABLE XXI-1 (cont'd)

STANDARD FREE ENERGIES OF FORMATION OF OXIDES, SULFIDES NITRIDES AND CARBIDES AT 1600 °C

No.	Reaction	ΔH° Cal per mole	ΔS° Cal per mole per deg K
	NITRIDES		
32	$Al(l) + 1/2\ N_2 = AlN(S)$	- 62,300	-30.1
33	$B(S) + 1/2\ N_2 = BN(S)$	- 27,700	-10.4
34	$3Be(l) + N_2 = Be_3N_2(S)$	-133,500	-40.6
35	$3Si(l) + 2N_2 = Si_3N_4(S)$	-209,000	-96.8
36	$Ti(S) + 1/2\ N_2 = TiN(S)$	- 80,300	-21.0
37	$V(S) + 1/2\ N_2 = VN(S)$	- 43,000	-21.4
38	$Zr(S) + 1/2\ N_2 = ZrN(S)$	- 82,200	-22.0
	CARBIDES		
39	$4Al(l) + 3C(gr) = Al_4C_3(S)$	- 35,700	-28.1
40	$Ca(g) + 2C(gr) = CaC_2(S)$	- 59,800	-21.6
41	$3Cr(S) + 2C(gr) = Cr_3C_2(S)$	- 8,550	+ 5.0
42	$2Mo(S) + C(gr) = Mo_2C\ (S)$	+ 4,200	+ 4.8
43	$Si(l) + C(gr) = SiC(S)$	- 38,400	- 8.5
44	$Ti(S) + C(gr) = TiC(S)$	- 57,300	- 2.5

TABLE XXI-2

Standard Free Energy of Solution of Various Elements in Liquid Iron(4)

Standard state is the infinitely dilute solution in pure liquid iron, referred to a 1 weight percent solution such that the activity of the added element is equal to its concentration in weight percent.

Element	γ^{o} 1873°K.	ΔF^{o} cal/mole
$Al(l) = \underline{Al}$	0.031	- 12,900 - 7.70T
$C(gr) = \underline{C}$		8,900 -11.10T
$Co(\ell) = \underline{Co}$	1	- 9.26T
$Cr(s) = \underline{Cr}$	1	4,350 -11.11T
$Cu(l) = \underline{Cu}$	8	9,300 - 9.40T
$\frac{1}{2}H_2(g) = \underline{H}$		7,640 + 7.68T
$Mn(l) = \underline{Mn}$	1	- 9.11T
$Mo(s) = \underline{Mo}$	1	6,280 -12.32T
$Ni(l) = \underline{Ni}$	1	- 9.21T
$\frac{1}{2}N_2(g) = \underline{N}$		860 + 5.70T
$\frac{1}{2}O_2(g) = \underline{O}$		- 27,980 - 0.70T
$Si(l) = \underline{Si}$	0.0072	- 29,000 - 0.30T
$\frac{1}{2}S_2(g) = \underline{S}$		- 31,520 + 5.27T
$Ti(s) = \underline{Ti}$	0.05	- 7,000 -11.00T
$V(s) = \underline{V}$	0.12	- 3,900 -11.07T
$W(s) = \underline{W}$	1	7,640 -13.62T
$Zr(s) = \underline{Zr}$	0.05	- 7,000-12.20T

The equilibria presented have been derived for the pure reactant phase, e.g. pure solid Al_2O_3. The relationships apply however, in all cases, and the deoxidizing power of an element may be computed under conditions of equilibrium with complex slag mixtures provided that the activity of the product in the slag is known. In fact, the deoxidizing power of an element increases as the activity of the compound formed decreases, as shown by Equation (XXI-2). The use of silicomanganese as a deoxidizer is an illustration of this fact. The deoxidation product is an iron-manganese-silicate slag in which the activities of the reaction products is much lower than what it would be if either pure silicon or manganese were used. In this manner, the deoxidation is more complete, and requires less deoxidizing material for the same degree of deoxidation. Application of vacuum to systems where a gaseous reaction product is formed, (e.g., CO), permits the reaction to reach a greater degree of completion.

These principles apply as well to the formation of nitrides, sulfides, carbides, and other insoluble compounds.

Interaction in Alloy Systems

The equations presented in Table XXI-2 have been developed for dilute, binary systems, and strictly apply only to these solutions. The activities in solutions which do not follow Henry's Law for the solute, or are multi-component, usually must be expressed as the product of a coefficient and concentration, and not concentration alone. The activity coefficient depends upon the degree to which the activity differs from the concentration. Activity is then expressed as:

$$a_M = f_M \, (\%\underline{M}) \qquad \text{XXI-22}$$

for solutions whose concentration is expressed in weight percent. If the standard state is defined as the infinitely dilute solution, and the activity is referred to a 1 weight percent solution, f_M is unity, i.e. the activity is equal to weight percent, when the solution follows Henry's Law for the solute.

The activity coefficient, f_M, depends upon the concentration of the solution, deviating from unity to a greater and greater extent as the solution becomes more concentrated in solute. The coefficient is also a function of alloy concentration, and is influenced by the presence of other elements, as well as increasing amounts of atoms of its own type. The atomic interactions of alloying elements in liquid iron and the factors which influence the activity coefficients in multi-component iron alloys has been discussed[6] and tabulated in the form of interaction parameters[6,7,8].

In solutions which are sufficiently dilute, Henry's Law behavior may generally be assumed. In addition, the influence of other alloying elements on the activity coefficients of the reacting elements is minimized in dilute solution. Under these conditions, activity coefficients may be assumed to be unity, and concentrations may be substituted for activities.

Precipitation Stoichiometry

The amount of reacting material which must be added to remove an impurity from solution consists of two parts. First, a portion of the material added reacts with the impurity and forms an insoluble precipitate which separates from the liquid alloy. A second portion is represented by the added material which remains in solution in sufficient quantity to satisfy the solubility product relationship.

Problem: A 100 ton ladle of steel at 1600°C contains 0.03 weight percent oxygen. Compute the amount of pure aluminum which must be added to reduce the oxygen content of the steel to 0.001 weight percent. Assume Henry's Law behavior for both aluminum and oxygen in solution, and that equilibrium conditions are reached.

Solution: The deoxidation constant for aluminum, assuming the conditions given above and that pure alumina is the reaction product, was determined for 1600°C. using Equation (XXI-21).

$$K = 4.7 \times 10^{-14} = (\%\underline{Al})^2 \, (\%\underline{O})^3$$

The equilibrium aluminum content is then:

$$(\%\underline{Al}) = \sqrt{\frac{4.7 \times 10^{-14}}{(0.001)^3}} = 6.85 \times 10^{-3}$$

The residual aluminum in solution in pounds is:

$$(100) \times (2000) \times \frac{6.85 \times 10^{-3}}{100} = 13.7 \text{ lb.}$$

The aluminum which reacted is given by the pounds of oxygen removed times the weight ratio in the reaction product, or:

$$\left(\frac{0.03 - 0.001}{100}\right) \times (100) \times (2000) \times \frac{(54)}{(48)} = 65.2 \text{ lb.}$$

The total aluminum required is given by the sum of the two amounts, or 78.9 lb.

Kinetics of Precipitation Reactions

The rate of approach to equilibrium for this type of refining reaction is controlled by nucleation and growth of the precipitate. A kinetic model may be derived in the same manner as that for phase separation processes which are discussed in the following chapter. The two refining processes are analogous, the phase separation process involving a reduction in solubility by a change in temperature, whereas the present consideration of precipitation involved changes in composition.

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CHAPTER XXII

PHASE SEPARATION

The refining of a metal by phase separation is accomplished by decreasing the temperature of a solution until the solubility limit of a dissolved constituent is exceeded. If the phase which separates out from a liquid is a solid, the process is termed crystallization. The phases are then separated by physical means, thus effecting a refining of the liquid, or recovery of a desired component from solution.

Thermodynamics

The equilibrium relationships for the separation of phases may be considered in terms of a phase transition and the distribution of the components of a binary solution between the phases. The transfer of one component from one phase to another may be expressed as:

$$(\text{Component 1})_{\text{phase I}} = (\text{Component 1})_{\text{phase II}} \qquad \text{XXII-1}$$

The equilibrium constant for the reaction above is:

$$K_1 = \frac{a_1^{II}}{a_1^{I}} \qquad \text{XXII-2}$$

A similar expression may be written for component 2 and the equilibrium relationship expressed by:

$$K_2 = \frac{a_2^{II}}{a_2^{I}} \qquad \text{XXII-3}$$

It is convenient to choose a standard state for component 2 such that a_2 approaches N_2 (mole fraction of component 2), as N_2 approaches zero in each phase[1]. Expressing the relationships above in terms of the activity coefficient and the mole fraction where a_1 is equal to N_1 if the major component (component 1 in this case) follows Raoult's Law, a valid assumption if the solution is dilute in component 2:

$$K_1 = \frac{(1 - N_2^{II})}{(1 - N_2^{I})} \qquad \text{XXII-4}$$

$$K_2 = \frac{N_2^{I}\gamma_2^{I}}{N_2^{II}\gamma_2^{II}} \qquad \text{XXII-5}$$

The equilibrium constants may be measured experimentally or calculated from free energy relationships. If the standard free-energy change for the transfer of a component from one phase to the other is known, then K_1 or K_2 may be determined from the relation: $\Delta F^{o} = -RT \ln K$. If the phase transition is defined for the solvent in terms of transition temperature, heat of transition, and known heat capacities for the phases involved, ΔF_1^{o} may be computed. The free-energy change for component 2 is not readily obtainable by this means since the pure solute generally does not undergo the same transition as the solvent. Thus K_2 must be determined empirically, and if values can be specified at two temperatures, an assumption of a linear relation between log K_2 and 1/T will permit extrapolation to other temperatures.[2]

Kinetics

The principle barrier to reaching equilibrium often manifests itself in the rate of nucleation of the separating phase. This is particularly true for crystallization processes, where large degrees of supercooling have often been noted. The surface energy between the precipitate and the solution must be considered particularly for solids, in addition to the differences in free-energies of the bulk phases.[3] The total free-energy change may then be expressed as:

$$\Delta F = a^3 \Delta F_v + 6a^2 \gamma \qquad \text{XXII-6}$$

where: ΔF_v is the bulk free-energy change

γ is the surface energy of a unit area of interface between the parent liquid and the crystal nucleus.

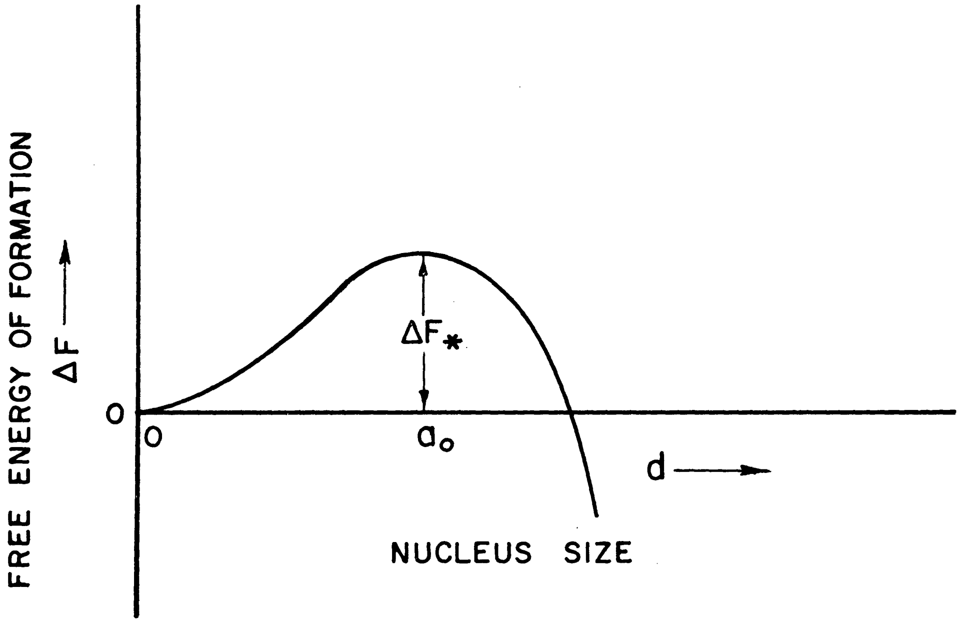
a^3, and $6a^2$ are the volume and surface area, respectively for a cube of side a, and it should be noted that these terms vary with the specific geometry of the nucleus.

The geometrical factors introduce a size effect into the problem and since ΔF_v is negative for a supercooled melt, these factors determine the critical size for a nucleus. When the nuclei are small, the positive term predominates, and the curve shown in Figure XXII-1 rises to a maximum as the size increases. A nucleus is stable if the size is greater than a_o, the critical nucleus size, since the free-energy decreases if the nucleus grows. The free-energy change for the formation of a nucleus of critical size is called the work of nucleus formation. The nucleus of critical size, a_o, is in unstable equilibrium with the parent phase since any change in its size results in a decrease in free-energy, and a tendency to either grow or disappear.

The work of formation is determined by a_o which may be evaluated by maximizing ΔF.

$$\partial(\Delta F)/\partial a = 3\, a^2 \Delta F_v + 12 a \gamma = 0 \qquad \text{XXII-7}$$

$$a_o = -4\gamma/\Delta F_v \qquad \text{XXII-8}$$



XXII-1. Free Energy of Nucleus Formation as a Function of Nucleus Size.

Substitution in Equation (XXII-6) gives:

$$\Delta F_{*} = \Delta F_{(a=a_0)} = -(4\gamma/\Delta F_v)^3 \, \Delta F_v + 6(4\gamma/\Delta F_v)^2 \gamma \qquad \text{XXII-9}$$

$$\Delta F_{*} = \beta \, \gamma/(\Delta F_v)^2 \qquad \text{XXII-10}$$

where the coefficient $\beta = 32$ for a cube. If the nucleus were spherical β would be equal to $16\,\pi/3$.

The value of ΔF which corresponds to the critical size represents an energy barrier that must be overcome by a nucleus before it is stable. The energy required can come only from momentary, local fluctuations of both concentration and energy. The energy fluctuations are statistical in nature and are of the usual kinetic type that gives rise to homogeneous reactions. The concentration fluctuation requires transport by molecular diffusion of the requisite number of molecules close enough to one another to form a nucleus large enough to equal or exceed the critical size. Becker[4] proposes the following equation for nucleation rate:

$$\frac{dN}{dt} = ce^{-Q/kT} \, e^{-A(T)/kT} \qquad \text{XXII-11}$$

where: dN/dt = nucleation rate, number/unit volume-unit time

Q = activation energy for diffusion

$A(T)$ = work required to form the surface of a nucleus

T = absolute temperature

c = a constant

k = Boltzman constant

The work of nucleation, $A(T)$, increases markedly with decrease in supersaturation and is infinite at the saturation point. The term $e^{-Q/kT}$ decreases with increase in supersaturation. The N versus T

curve thus has a pronounced maximum that corresponds to a definite supersaturation. However, theoretically if time enough is allowed, homogeneous nucleation will eventually occur at any supersaturation. The presence of foreign particles or of seed crystals can appreciably increase the nucleation rate by innoculation. The alteration of surface energies, caused for example by the presence of trace amounts of surface active elements, can also drastically affect the rate of nucleation. These effects occur because of the change in the surface energy term of the nucleation rate equation.

A more complete discussion of the kinetics of phase precipitation is provided in the Supplementary References[2-9].

It may be concluded from the foregoing discussion that heterogeneous nucleation caused by the presence of seed crystals or innoculating agents which promote nucleation will occur prior to homogeneous nucleation. This is desirable in phase separation processes since a rapid nucleation of the precipitating phase promotes the kinetics of phase separation, and prevents nucleation of the precipitant from becoming rate limiting. In practice, it is often necessary to "seed" the melt with foreign particles to promote heterogeneous nucleation. Agitation in the form of vigorous stirring or vibrating techniques have also been used to promote nucleation.

If growth of the precipitate is rate limiting, the kinetics of phase separation may be described in terms of the rate model developed for liquid-liquid extraction in Chapter XX.

Processing Operations - Lead-Silver System

Recovery of silver from lead may be accomplished by cooling the silver-containing lead bath. Consider a lead-silver alloy containing, 20 weight percent silver. As shown in Figure XXII-2, lead-silver solutions will precipitate out a solid of very high silver content on cooling. The composition of the liquid solution will follow the liquidus line of the diagram if equilibrium conditions are maintained. On cooling, the alloy will begin to precipitate a silver solid solution at a temperature of 540°C. and will continue to do so, until the eutectic point is reached at 2.5 percent silver and 304°C. At this point, the liquid can be filtered or the solid skimmed off (the lighter silver floating on the liquid bath) resulting in $[(20 - 2.5)/20] \times 100 = 87.5$ percent recovery of the silver.

Further purification can be accomplished by the Parkes Process in which silver is removed in a silver-zinc layer when zinc is added to the lead. This technique is also a phase separation process except that it is more accurately described in terms of precipitation reactions as described in the previous chapter.

Zinc Recovery by Phase Separation

An example of the commercial application of phase separation is in the recovery of zinc from the zinc-lead blast furnace operating at Avonmouth, England[10]. This process is shown schematically in Figure XXII-3. Ores which are high in zinc are smelted in a lead blast furnace, producing a stack gas containing up to 6% zinc. The stack gases are passed through a splash-condenser containing lead which absorbs the zinc from the vapor phase. It is reported that under

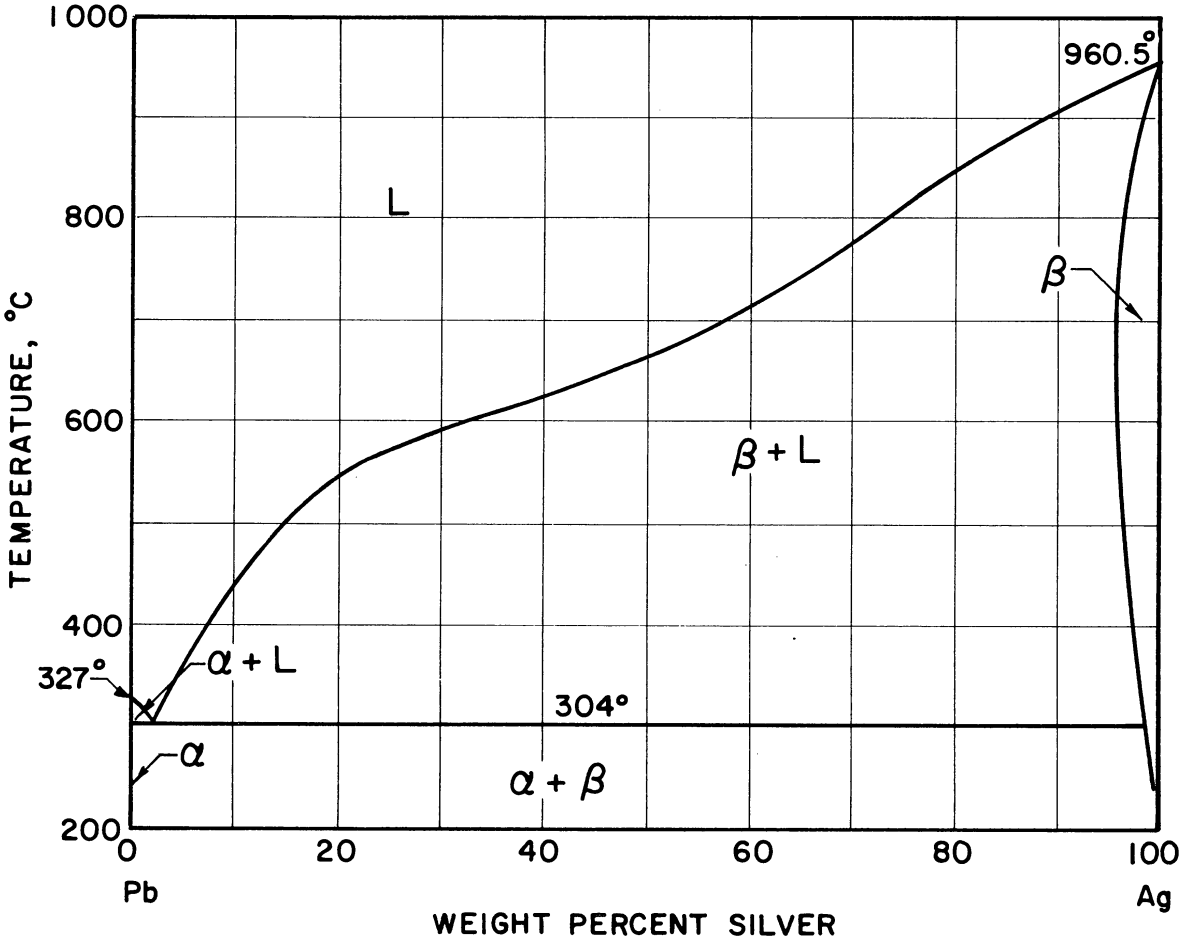


Figure XXII-2. Phase Diagram for the Lead-Silver System.

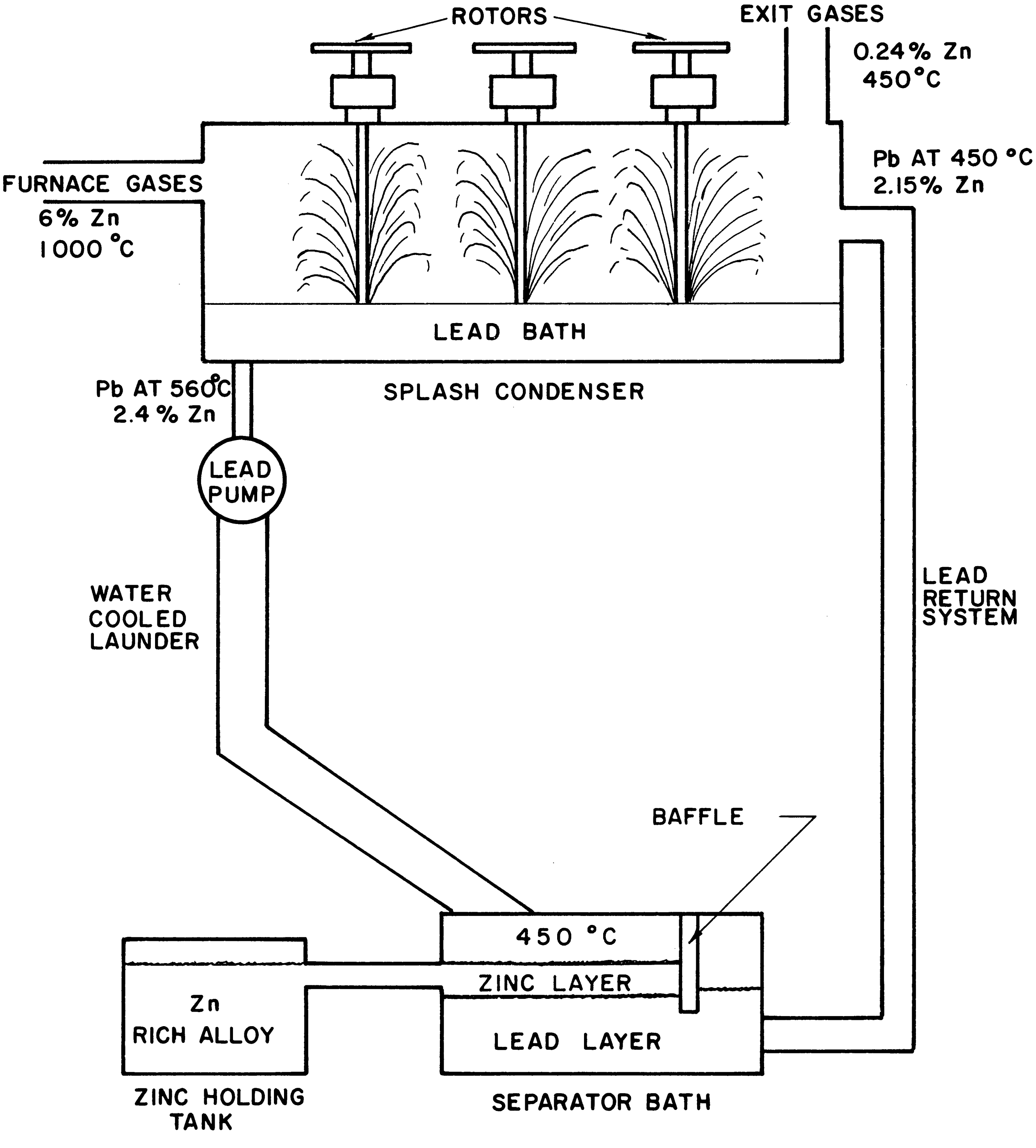


Figure XXII-3. Schematic Diagram of Zinc Recovery System for Zinc-lead Blast Furnace.

typical conditions the gas entering the condensers contains 5.9 percent zinc at a temperature of 1000°C. The gas leaves the condenser at a temperature of 450°C. and contains about 4 percent of the entering zinc. The lead enters the condenser at 450°C. and leaves at about 560°C. It is saturated with zinc on entering, 2.15 weight percent. During the condensation, the lead is heated and dissolves an additional 0.25 percent zinc. The lead is then circulated through a cooling launder. The concentration of zinc 2.4 percent, is far below the saturation point on exiting from the condenser, 4.4 percent at 560°C. However, on cooling essentially pure liquid zinc begins to precipitate out from the lead at 470° C. where the solution becomes saturated. Cooling is continued to 450°C. and the additional 0.25 percent absorbed in the condensers separates out. The upper liquid layer of zinc is then separated by means of a weir, and the underflow of lead-rich alloy is recirculated.

Engineering Design

The major considerations of a phase separation which concern the engineer are:

1. The yield of a given product.
2. The purity of the product.
3. The energy requirements.
4. The rate of production.

Process Yield

The yield of the product may be estimated by constructing a material balance for the system, assuming that equilibrium conditions prevail. This would represent the maximum yield, a quantity which is given in pounds by:

$$Y = W_o \frac{c_2^I - c_2^0}{c_2^I - c_2^{II}} \qquad \text{XXII-12}$$

where:

W_o is the initial weight of the charge in pounds

c_2^I is the equilibrium concentration in weight percent of component 2 in the parent phase at the lower temperature.

c_2^0 is the concentration in weight percent of component 2 in the parent phase initially.

c_2^{II} is the equilibrium concentration in weight percent of component 2 in the precipitated phase at the lower temperature.

Equation (XXII-12) is an expression of the "lever-rule". Mole fractions may be substituted for weight percentages and N_o, the total number of moles of initial solution, substituted for W_o. The yield is then expressed in moles, and the weight may be computed from the molecular weights of the solute and solvent and the concentrations in the product.

When the process involves a highly volatile solvent, or reactions occur between the lining of the process container and the material being processed, a correction must be made to the yield relation given above for the losses.[11]

Purity of Product

The purity of the product for the equilibrium case is given directly from the phase diagram. In practice, the adherence of the parent liquid to the precipitated crystals, or the entrainment of one phase within the other often decreases the purity of the recovered material. The purity can usually be improved by repeating the phase separation on the product. In the case of crystals precipitated from aqueous or organic solutions, washing with fresh solvent can greatly improve the purity.

Thermal Requirements

The energy requirements for a phase separation can be calculated from a heat balance on the process. The cooling energy represents heat which must be removed from the system and is given by the sum of the sensible heat change in the solution, heat evolved during the separation of phases, (a quantity which may be either negative or positive, and is often approximated by the heat of solution for dilute solutions whose composition does not vary greatly during the operation), minus the heat losses to the surroundings, and any other cooling effects, e.g., vaporization of the solvent.

Process Kinetics

The rate at which a phase separation can be carried out may be limited either by the kinetics of the process, or the capacities of the equipment, or both may play a role. The kinetics of nucleation have been briefly introduced in a previous section, and may be applied to the case where the rate limiting step is the nucleation of the second phase. The growth of the phase may also be rate limiting, in which case the relationships of Chapter XX may be used to define the process rate.

The ability of the equipment to extract heat from the solution at a rapid rate may be a primary factor in the rate of the process. Also the removal of the material from the equipment, or the charging methods i.e., material handling, may limit the operation. Consideration of these factors are of major importance in the engineering design of phase separation processes.

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CHAPTER XXIII

DEGASSING OPERATIONS

One of the principal quality problems that faces the metalmaker in producing a suitable product is that of control of gases. Hydrogen is a particularly troublesome gas causing bleeding ingots, embrittlement, and low ductility as well as the presence of blow holes. Nitrogen is also a gas which may have a desirable or undesirable effect on the properties of a metal, particularly steel, depending upon the composition, subsequent treatment, and the use of the product. Oxygen, of course, is a principal refining agent, and, consequently, plays a role in determining the properties of metals. In addition to these simple gases, there are also complex gases, those which contain more than one type of atom in the molecule; principally, CO, CO_2, and H_2O. In the design of processes to control these gases in metals, solubilities, rates of solution, and the chemical reactions involved in their formation or decomposition in the metal are required, particularly in the liquid state. Much of this data is presently available, and an attempt will be made in this chapter to show its application in the design of degassing operations as a refining process.

Fundamentals of Gas-Metal Reactions

The solubility of a gas in a metal is a function of the pressure of that gas above the liquid metal. The solubility of a diatomic gas, nitrogen for example, is proportional to the square root of the pressure of nitrogen, which is in equilibrium with the melt. This relationship has come to be known as Sieverts' Law. It follows directly from consideration of the equilibrium of the reaction:

$$1/2\, N_2 = \underline{N} \qquad \text{XXIII-1}$$

where the equilibrium constant may be expressed as:

$$K_1 = \frac{a_{\underline{N}}}{(P_{N_2})^{\frac{1}{2}}} = \frac{f_N(\%\underline{N})}{(P_{N_2})^{\frac{1}{2}}} \qquad \text{XXIII-2}$$

Rewriting the expression for the equilibrium constant, and taking the activity coefficient of nitrogen in pure liquid iron as being equal to one:

$$\%\underline{N} = K_1 \sqrt{P_{N_2}} \qquad \text{XXIII-3}$$

A similar relationship may be written for hydrogen.

The rate-limiting step for the removal of gas from a liquid metal is generally diffusion through a boundary layer in the metal. The rate process for the removal of a gas from a liquid metal may then be written in terms of the diffusion model given in Chapter IV.

The reactions between gases dissolved in metals and other constituents in solution are expressed in terms of the reactions taking place, and equilibrium constants may be written for them. For example, the equilibrium partial pressure of CO over liquid steel is determined by the product of the carbon and oxygen activities in the liquid metal. This may be seen from the expression:

$$\underline{C} + \underline{O} = CO \qquad \text{XXIII-4}$$

Where the equilibrium constant may be written as:

$$K_4 = \frac{P_{co}}{a_{\underline{c}} \cdot a_o} \qquad \text{XXIII-5}$$

This expression may be rewritten in ~~the form:~~

$$P_{CO} = K_4 \cdot a_c \cdot a_o \qquad \text{XXIII-6}$$

which indicates that the partial pressure of CO in equilibrium with the steel is determined by the equilibrium constant and the product of the activities of carbon and oxygen in solution.

One might also consider the solubility product of a compound which contains the atomic specie of a gaseous component. For example, the solubility product of aluminum nitride is given by the reaction:

$$AlN = \underline{Al} + \underline{N} \qquad \text{XXIII-7}$$

where the equilibrium constant may be expressed as:

$$K_7 = \frac{a_{\underline{Al}} \cdot a_{\underline{N}}}{a_{AlN}} \qquad \text{XXIII-8}$$

Combining this expression with Equation (XXIII-3), one can compute the partial pressure of nitrogen in equilibrium with a melt containing a given weight-per cent aluminum, and in contact with aluminum nitride at a given activity, provided the activity coefficients for the solution are known.[1] The reaction would be expressed as:

$$1/2\ N_2 + \underline{Al} = AlN \qquad \text{XXIII-9}$$

where the equilibrium relationship is given by:

$$K_9 = \frac{K_1}{K_7} = \frac{a_{AlN}}{(P_{N_2})^{\frac{1}{2}}\ f_{Al} \cdot (\%Al)} \qquad \text{XXIII-10}$$

The activities of constituents in solution are influenced by the presence of other alloying elements. The magnitude of this influence is determined by the interaction parameter (See Chapter XXI), which is defined as[2]:

$$e_n^j = \frac{\partial[\log f_n]}{\partial(\%\ j)}$$

where n is the alloying element under consideration, and j is another alloying element in solution whose presence influences the activity coefficient of n. A complete list of the thermodynamic interaction parameters of elements in liquid iron has been prepared and correlated with the periodic table.[3]

Inert Flush Degassing

Inert flush degassing is a process carried out by bubbling an inert or insoluble gas through the liquid metal. Since the solubility of the gas in the liquid metal is a function of the partial pressure of that component in the gas phase with which the metal is in contact, the presence of an atmosphere which is very dilute in the dissolved gas and sufficient time, will provide a means for eliminating the dissolved gas. The removal of dissolved gas from liquid metal involves diffusion through a boundary layer in the melt and the reaction of evaporation from the surface, and consequently, any process which shortens the diffusion path or provides a greater surface area should provide a more rapid means for reducing the dissolved element. The blowing of an inert flush gas through the liquid metal in finely dispersed bubbles is such a process.

An Equilibrium Process

The process engineer is interested in the rate at which inert flush degassing will remove a dissolved gas. If one considers that the flush gas is in equilibrium with the melt when it leaves the metal surface, that is, that the partial pressure of dissolved gas in the exiting bubble is equal to the equilibrium partial pressure for the concentration of dissolved gas in the melt at that instant, one may write the following relationship:

$$-dN_G = (dN_F + dN_G)\frac{P_G}{(P_G + P_F)} \qquad \text{XXIII-11}$$

where N_G is the liters of dissolved gas, N_F the liters of flushing gas, and P_G and P_F represent the respective partial pressures in the exiting gas bubble. Since the total pressure on the system is one atmosphere, $P_G + P_F$ is equal to 1, and Equation (XXIII-11) may be rewritten as:

$$dN_F = -dN_G \left(\frac{1+P_G}{P_G}\right) \qquad \text{XXIII-12}$$

Converting from liters of dissolved gas to parts per million by weight:

$$dN_F = -\left(\frac{20.24W}{M}\right)\left(\frac{1+P_G}{P_G}\right) dC_G \qquad \text{XXIII-13}$$

where W is the tons of metal and M is the molecular weight of the dissolved gas. For the case where the dissolved gas is diatomic the equilibrium pressure of dissolved gas, P_G, is related to the concentration of dissolved gas by Sieverts' Law:

$$C_G = K_G \, (P_G)^{\frac{1}{2}} \qquad \text{XXIII-14}$$

where the concentration is expressed in parts per million and the pressure in atmospheres. The Sieverts' Law constant is given in the units, $\text{ppm}/(\text{atm})^{\frac{1}{2}}$. The partial pressure of dissolved gas is then:

$$P_G = \left(\frac{C_G}{K_G}\right)^2 \qquad \text{XXIII-15}$$

Equation (XXIII-13) may be integrated in the form:

$$\int_0^{V_F} dN_F = -\left(\frac{20.24W}{M}\right) \int_{C_o}^{C} dC_G + K_G^2 \frac{dC_G}{C_G^2} \qquad \text{XXIII-16}$$

The volume of flush gas in liters, V_F, required to reduce the dissolved gas content in ppm from C_o to C is:

$$V_F = \frac{20.24\,W}{M} (C_o - C)\,(K_G^2 + C\,C_o)\,/C\,C_o \qquad \text{XXIII-17}$$

Boundary Layer Model

There is some evidence[4] to indicate that the bubble is not in equilibrium when it leaves the liquid metal. The transfer of dissolved gas from the liquid melt to the inert flush bubble is controlled by diffusion of the dissolved specie through a boundary layer surrounding the bubble. Since the diffusion coefficient is finite and the residence times for bubbles are relatively small, it is quite conceivable that the exiting bubble would not have sufficient time to reach equilibrium. If it is assumed that the melt remains homogeneous throughout the flush process, and that the concentration of dissolved gas in the flush bubble exiting from the melt is quite small, i.e., that the concentration gradient through the boundary layer film surrounding the bubble is essentially given by the concentration of the bulk metal divided by the boundary layer thickness, a reasonable model may be derived. It should be noted that this selection of the concentration gradient through the boundary layer film assumes that the concentration in the boundary layer at the bubble surface is zero. Under these conditions, the concentration gradient, approximated as $\Delta c/\Delta x$, is equal to $(c - 0)/\delta$. The kinetics of inert flush degassing are described by the relation:

$$-\frac{dc}{dt} = \frac{D\ A_B}{\delta\ V_M}\ F\ t_R\ c \qquad \text{XXIII-18}$$

where D is the diffusion coefficient of the atomic specie of the gas in the metal, A_B is the average area of a gas bubble, V_M is the volume of the liquid metal phase, F is the flow rate of the flush gas, t_R is the residence time of the average gas bubble, and c is the instantaneous concentration of dissolved gas in the metal.

The expression integrates to the form:

$$\log\left(\frac{c_o}{c}\right) = k'\ t \qquad \text{XXIII-19}$$

where k' is a constant which may be evaluated from the factors given on the right-hand side of Equation (XXIII-18). In general, these factors may be determined from the geometry of the degassing equipment. It should be noted that t_R, the residence time, is a constant which represents the time required for a gas bubble to leave the source which is injecting the flush gas and rise to the surface of the melt.

The boundary layer model, which expresses the concentration of dissolved gas in the melt in the general form of Equation (XXIII-19), is in excellent agreement with the experimental results[4] shown in Figure XXIII-1.

Calculation of Residence Time

The residence time may be computed by assuming that the bubble is a sphere and writing a force balance about the bubble. The forces on the bubble are the bouyant force, its weight and the friction force caused by viscous drag. Thus:

$$F = ma = wg - mg - F_d \qquad \text{XXIII-20}$$

where g is the acceleration due to gravity, w is the mass of fluid displaced by the bubble, i.e., having the same volume, and m is the mass of the bubble. Hence, wg is the buoyant force on the bubble, mg is the gravitational force, and F_d is the resisting force caused by friction effects in the viscous fluid.

or:

$$\frac{dv}{dt} = \frac{\rho_L - \rho_B}{\rho_B} g - \frac{3 f_D \rho_L v^2}{4d \rho_B} \qquad \text{XXIII-21}$$

where d is the diameter of the bubble and ρ_B its density, v is the velocity of the bubble in the vertical direction, ρ_L is the density of the liquid metal, and f_D is the drag coefficient which is given as a function of Reynolds number in Table XXIII-1.

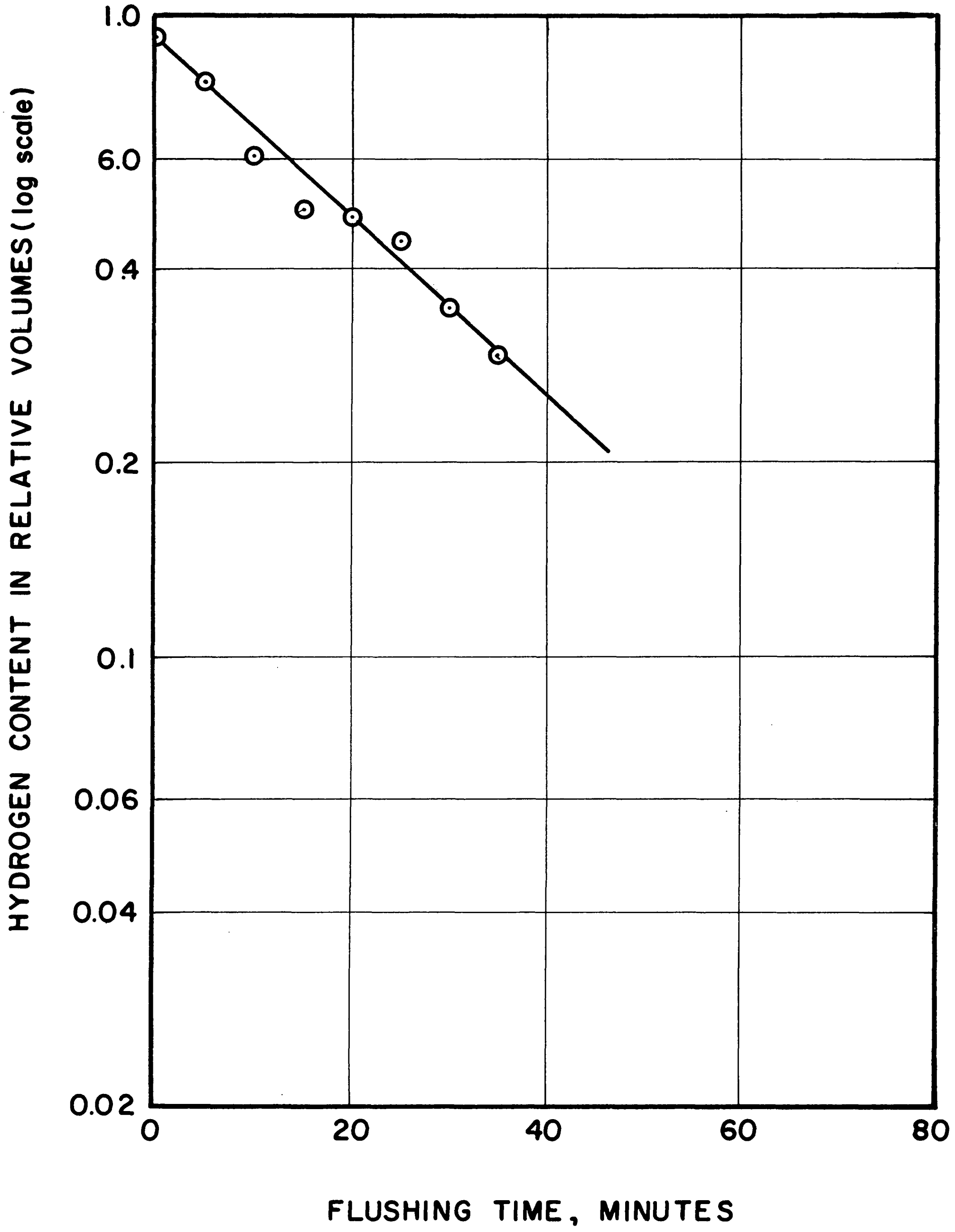

Figure XXIII-1. Removal of Hydrogen from Liquid Steel by Flushing with Argon.

TABLE XXIII-1

Relationship Between Reynolds Number and Drag Coefficient for Bubble Flow*

f_d	R_e
10^7	2×10^{-6}
10^6	2×10^{-5}
10^5	1.8×10^{-4}
10^4	1.75×10^{-3}
10^3	2×10^{-2}
10^2	1.8×10^{-1}
10	2.0
1	35
.2	200
.18	300
.2	350
.3	400
.9	900
2.5	2000
2.5	10,000

* Reported by David Taylor Model Basin, Department of the Navy

If a bubble is assumed to instantaneously reach a terminal velocity and to rise with no rapid changes in acceleration, the velocity at any point is given as:

$$v = - \frac{dh}{dt} = \left[\frac{4(\rho_L - \rho_B) g\ d}{3\rho_L\ f_D} \right] \qquad \text{XXIII-22}$$

Where h is depth in the melt, and the residence time, t_R, is given by the integral:

$$t_R = \int_H^0 \frac{-dh}{\left[\frac{4(\rho_L - \rho_B) g d}{3\rho_L f_D} \right]} \qquad \text{XXIII-23}$$

where H is the depth at which the flush gas is discharged.

Equation (XXIII-23 may be evaluated in either of two ways. First, average values for the density of the gas and the diameter of the bubble may be selected, and the average velocity computed using a trial and error solution involving the drag coefficient and the Reynolds number. A more rigorous approach may be taken. The density of the gas may be expressed as a function of atmospheric pressure and depth in the melt, and perhaps temperature as well, since the bubble is heated during is passage through the liquid metal. The diameter of the bubble is expressed in terms of the density and mass of gaseous material in the bubble. These may be substituted in the integral of Equation (XXIII-23) which is then evaluated graphically. Alternatively, using these expressions for bubble diameter and density, the velocity may be determined at several depths in the melt using Equation (XXIII-22). The average of these values would give a reasonable value for the velocity up through the melt, at least one which is of higher reliability than one calculated using the first procedure outlined. In the event that the velocity remains essentially constant, the assumption of neglegible acceleration is valid, and the residence time is given by the expression:

$$t_R = \frac{H}{v} \qquad \text{XXIII-24}$$

Vacuum Degassing

An operation which is capable of producing liquid metals containing extremely low concentrations of dissolved gases is that of vacuum degassing. The liquid metal is held in a closed container under extremely low pressures. The mechanism by which the dissolved gases are removed is essentially the same as that previously described, diffusion through a boundary layer at the surface and evaporation from that surface into the vapor space above. Since the partial pressure of dissolved gases above the surface of the melt is extremely low in the vacuum and remains that way throughout the operation, this is a very effective way of removing dissolved gases.

Assuming the rate controlling step to be diffusion of atomic species of the gaseous component through a boundary layer in the metal, the kinetics of vacuum degassing processes may be described by the equation:

$$\frac{dc}{dt} = -\frac{D\ A}{\delta\ V}\ c \qquad \text{XXIII-25}$$

where A is the area of the gas-metal interface, generally taken as the cross-sectional area of the crucible or furnace hearth, V is the volume of the melt, and c is the concentration of dissolved gas. Since the concentration at the gas-metal interface is assumed to be in equilibrium with the gas phase, in this case a vacuum, the concentration gradient is given by the ratio, c/δ. If the process is carried out at reduced pressures rather than under a vacuum, the gradient is given by $(c - c_e)/\delta$, where c_e is the concentration of dissolved gas in equilibrium with its reduced partial pressure in the process atmosphere.

Equation (XXIII-25) integrates to:

$$\text{Log}\ \left(\frac{c_o}{c}\right) = \frac{D\ A}{2.3\ \delta\ V}\ t \qquad \text{XXIII-26}$$

It should be noted that according to this model, as long as the reaction taking place at the surface of the melt is much more rapid than the rate of diffusion through the liquid boundary layer, the degassing rate is independent of the molecular form of the gas specie formed in the vapor space above the melt.

Figure XXIII-2 shows the concentration of hydrogen in a melt of steel as a function of time under vacuum[5]. The slope of the curve, k', i.e., the reaction rate constant for degassing, is given by the coefficient of Equation (XXIII-26):

$$k' = \frac{D\ A}{2.3\delta\ V} \qquad \text{XXIII-27}$$

Assuming that D equals 6×10^{-3} cm^2/min, δ equals 0.003 cm., and that $\frac{A}{V}$ is 50 cm, the predicted rate constant is:

$$k' = \frac{6 \times 10^{-3}}{(2.3)(0.003(50)} = 0.017 \ \text{min}^{-1}$$

which is in approximate agreement with the average slope of the line in Figure XXIII-2, about 0.02 minutes^{-1}.

The desulfurization of a liquid 80% Ni-20% Co alloy[6] under a vacuum of 10^{-5} atmospheres is shown as a function of time in Figure XXIII-3. The melt was 10 centimeters deep, and if a diffusion coefficient for sulfur of 3×10^{-5} cm^2/sec and a boundary layer thick-

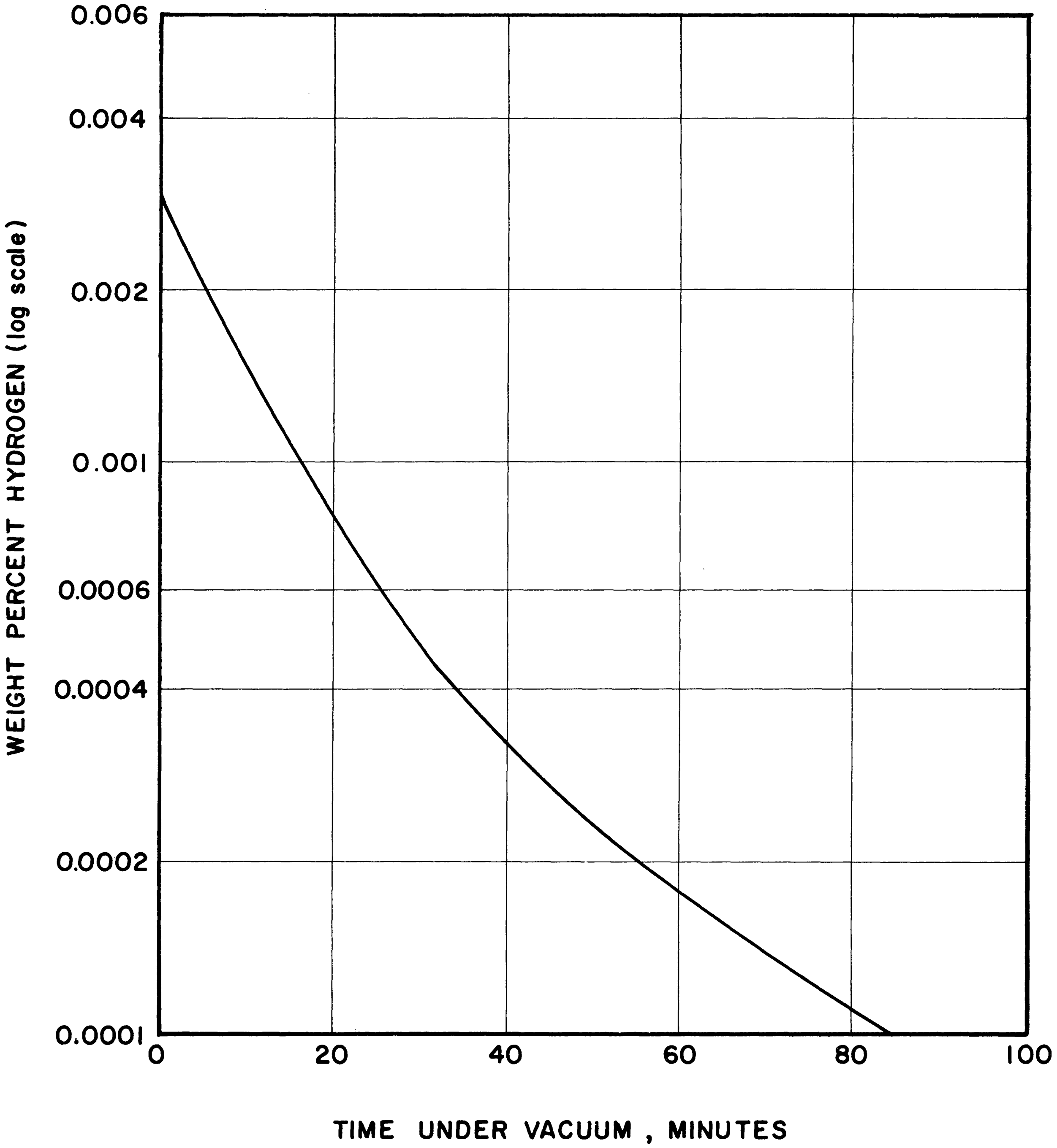

Figure XXIII-2. Vacuum Degassing of Liquid Iron in Magnesia Crucible.

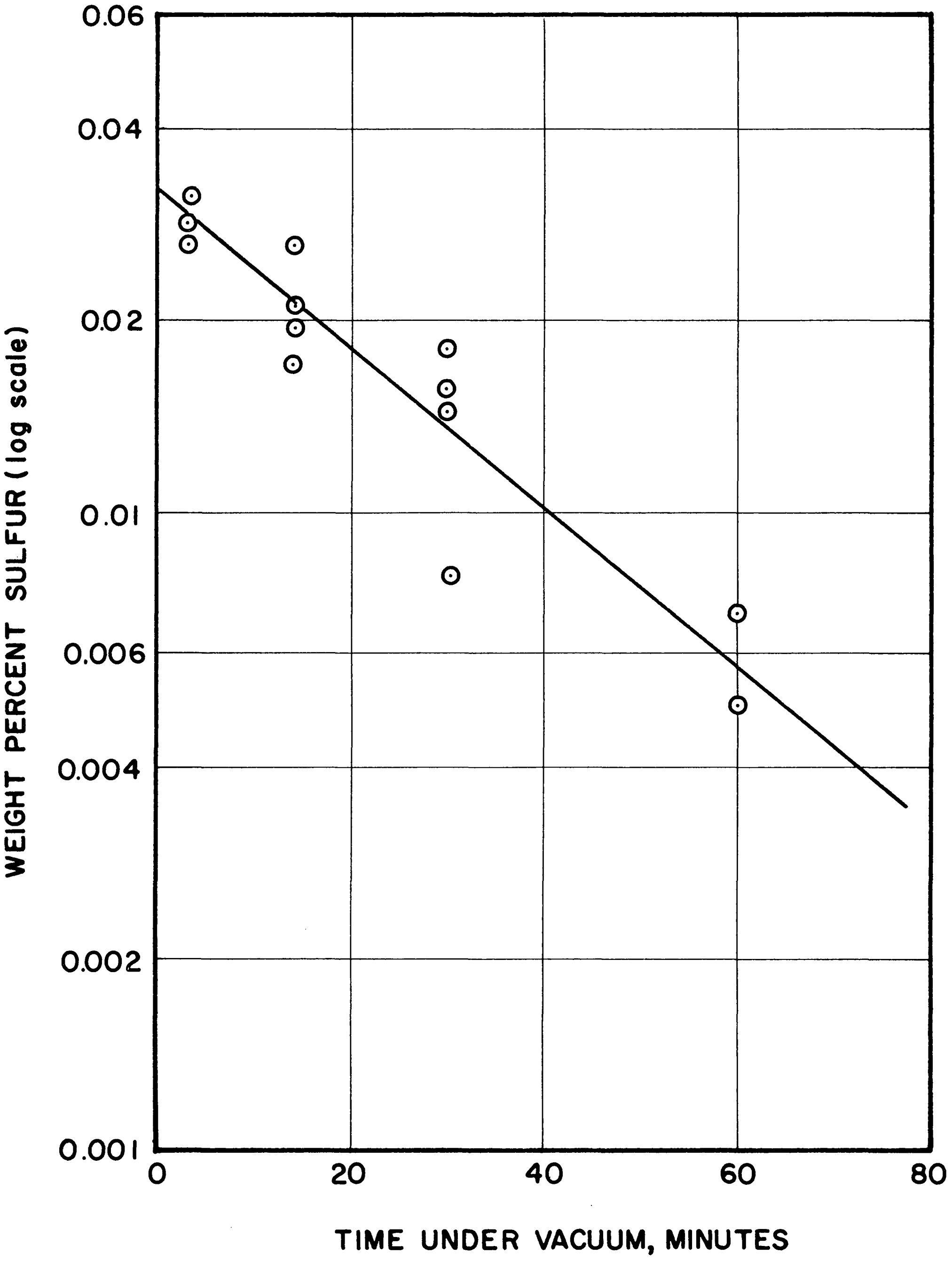

Figure XXIII-3. Desulfurization of an 80%Ni- 20%Co Alloy at 1530°C by Vacuum Treatment.

ness of 0.003 centimeters are selected, the estimated rate constant is:

$$k' = \frac{3 \times 10^{-5}}{(2.3)(0.003)(10)} = 4.3 \times 10^{-4} \text{ sec.}^{-1}$$

An average observed value of 2.1×10^{-4} seconds $^{-1}$ is in reasonable agreement with the predicted result.

These examples serve to illustrate the general validity of the assumption that diffusion through a boundary layer in the melt is the rate controlling step in the kinetics of vacuum degassing processes at high temperatures.

Other Degassing Processes

Numerous vacuum degassing processes have been proposed which attempt to produce a larger gas-metal surface area, and consequently, an increased rate of degassing. This is particularly important in the treating of liquid metals since the metal temperature decreases during the operation and a limited amount of time is available for it. One such process is the Dortmund-Hörder process which was described in Chapter V (Figure V-1).[7,8]

Recently, a new process has been developed in Germany called the Ruhrstahl-Heraus Continuous Vacuum Process. This is used exclusively in ladle degassing. The ladle of molten steel is placed in a pit in the teeming shed, and the vacuum apparatus positioned by an over-head crane. Tubes are lowered into the melt while the vacuum chamber is being pumped out by a multiple stage pumping system. Argon is introduced into one of the tubes, and the liquid steel moves up in this tube. The metal then splashes into the vacuum chamber where it is degassed. The time required to degas 100 tons of liquid steel is 15-20 minutes, and the temperature drop during this period is only about 30° C. If necessary, it is possible to heat the liquid steel by auxiliary equipment during the vacuum treatment[9,10]. A schematic diagram of the process is presented in Figure XXIII-4.

Knowing the volume of argon introduced and the geometry of the system, it should be possible to predict the decrease in concentration of dissolved gases in the liquid metal, providing one assumes something about the degree of degassing performed in the vacuum chamber.

Several other vacuum degassing techniques include vacuum degassing in the ladle, a process devised by A. Finkl and Sons Company, Chicago[11]. Vacuum stream degassing is another method of bringing more of the surface of the melt in contact with the vacuum. In this process a ladle of steel to be degassed is placed over a vacuum chamber and the liquid metal is permitted to flow into the vacuum chamber. The reduced pressure causes the gases to diffuse from the metal, which is received in another ladle below from which it can be repoured into an ingot mold. The thin stream of molten metal allows an excellent chance for the vacuum to degas the melt quickly and efficiently, and results by this method have been as low as two parts per million residual hydrogen[12]. Other vacuum degassing techniques include the consumable electrode melting process in which an ingot of material is simultaneously melted and degassed in a vacuum.

Another effective method of controlling dissolved gases particularly for oxygen and nitrogen is that of adding a scavenging element such as titanium or zirconium. These elements form stable nitrides or oxides which are insoluble in liquid metals. The principles involved here are the same as those outlined in Chapter XXI .

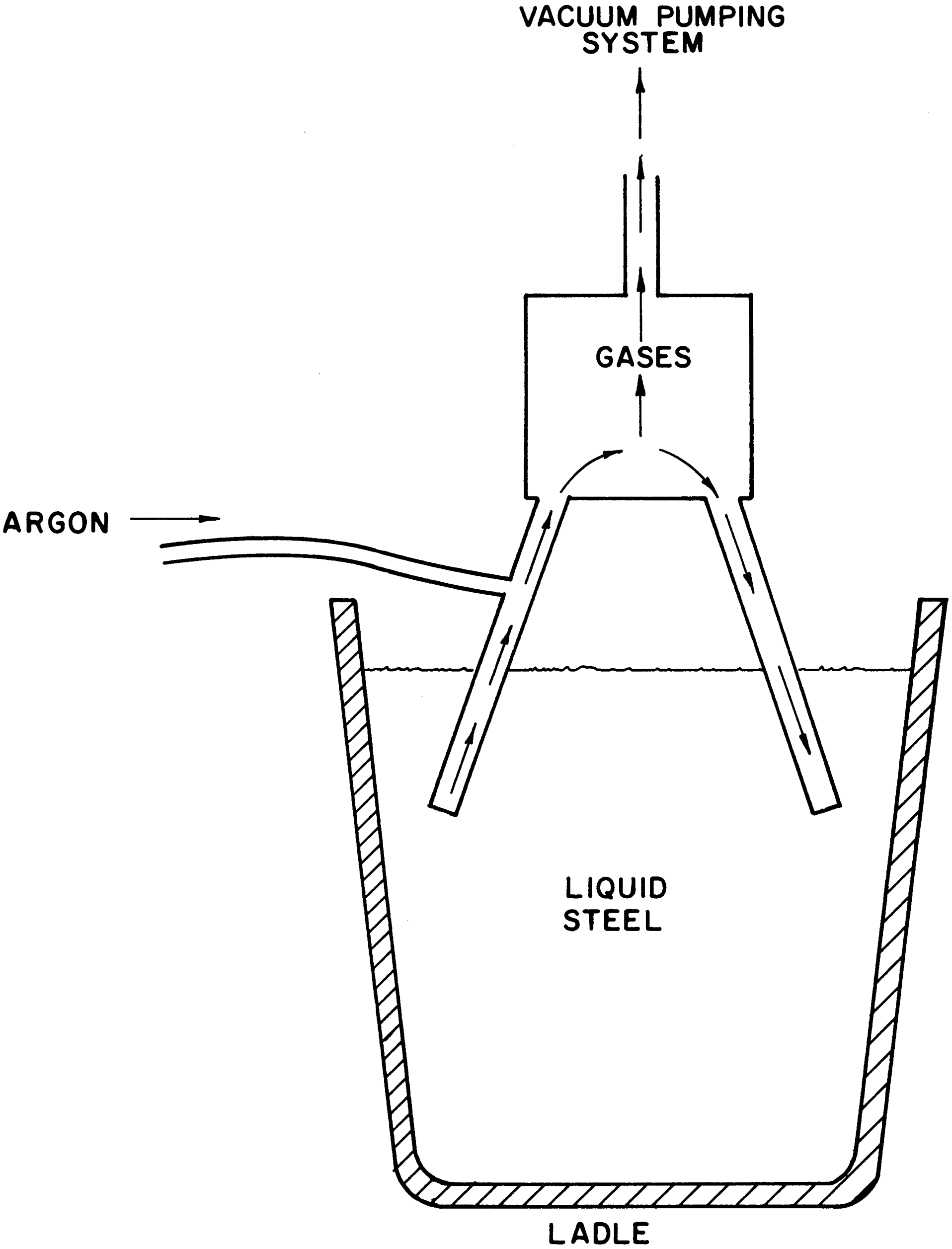

Figure XXIII-4. Schematic Diagram of Vacuum-Flow Steel Degassing Process.

Inert flush degassing may also be accomplished by placing a volatile solid in the liquid melt which then forms purging gases that are evolved in the bulk of the metal. An engineering analysis of the effectiveness of such a method may be accomplished in a manner similar to that outlined above under Inert Flush Degassing.

The high effectiveness of the methods outlined here and the perfection of the processes, as well as the development of economic equipment for accomplishing them will undoubtedly see a greater and greater use of degassing methods as a refining operation in the metallurgical industries.

Temperature Drop of the Melt During Degassing

The temperature drop of the melt during degassing may be computed directly by a consideration of the radiation and convection losses from the metal and its container during the degassing operation. The principal source of heat loss especially for steels is by direct radiation from the exposed metal surfaces. The heat effect caused by the removal of the dissolved gas from solution and in inert flush degassing the sensible heat lost to the flush gases is also negligible in comparison. The time available for the degassing operation may then be computed directly by considering the heat losses and any energy which may be supplied to the operation.[13]

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Part V

INTEGRATED OPERATIONS

CHAPTER XXIV

ELECTRONIC COMPUTERS IN PROCESS ENGINEERING

One of the major developments in the rapid advances made in the scientific field in the last 15 years has been the perfection of the electronic computer in both its analog and digital forms. The importance of electronic computers in the engineering of systems has been established, and they shall undoubtedly take preeminence as the major tool of the process design engineer.

There are two basic types of large-scale calculating machines in use today, the analog or continuous variable machine and the digital or discrete variable machine. An analog computer is a physical system, mechanical, electrical or optical, which is designed in such a way that the variables of the system satisfy the same mathematical laws as do the variables of the problem of interest. The physical process of computation is replaced by a measurement of the physical quantities corresponding to the values of the unknown variables. Digital computers, in contrast, perform their operations by counting in a manner similar to a desk calculator.

The Digital Computer

The large-scale digital calculator will perform only the simplest types of operations. First of all, it will read; i.e., assimilate information which is supplied to it on punched cards, punched paper tape, magnetic tape, or by other similar techniques. Secondly, it will remember what it has read. The memory cells of most digital computers consist of magnetic cores, mercury delay lines, cathode-ray-tubes, magnetic drums, banks of relays, or electrostatic storage tubes. A relay computer remembers information by having certain relays in an energized condition while others are in the unenergized condition. Information is stored in a similar yes-no manner by other basic electrical components. Thirdly, the digital machine will perform arithmetical operations. Most computers will add, subtract, multiply, and divide. By combination of these basic operations, subroutines may be developed to take roots, raise numbers to powers, or evaluate other commonly used functions. Fourth, the large-scale digital computer may exercise choice. It is able to follow a set of logical expressions, choosing between one set of operations and another on the basis of relative magnitudes of quantities stored within its memory. Finally, the computer can write. Based on instructions given to it, it may record on punched cards, tape, or other output devices, the values of quantities stored within its memory.

Figure XXIV-1 illustrates the performance of a digital computer. The computer reads data and instructions which are presented to it, and then performs the operations upon the data according to the instructions. In performing these operations, the computer may use any of the five facilities which it possesses. These facilities are indicated in the square of Figure XXIV-1 which shows the computer as a black box. A detailed examination of the internal workings of a digital computer as well as references on the subject has been prepared by Goode and Machol[1]. The output of the computer is then the numerical results called for by the original machine instructions.

A simple example may serve to illustrate the way in which a digital computer may be used. Suppose one wishes to evaluate the polynomial:

$$R = a_o + a_1x + a_2x^2 + a_3x^3 + \dots\dots + a_nx^n \qquad \text{XXIV-1}$$

at each integer value from 0 to 100.

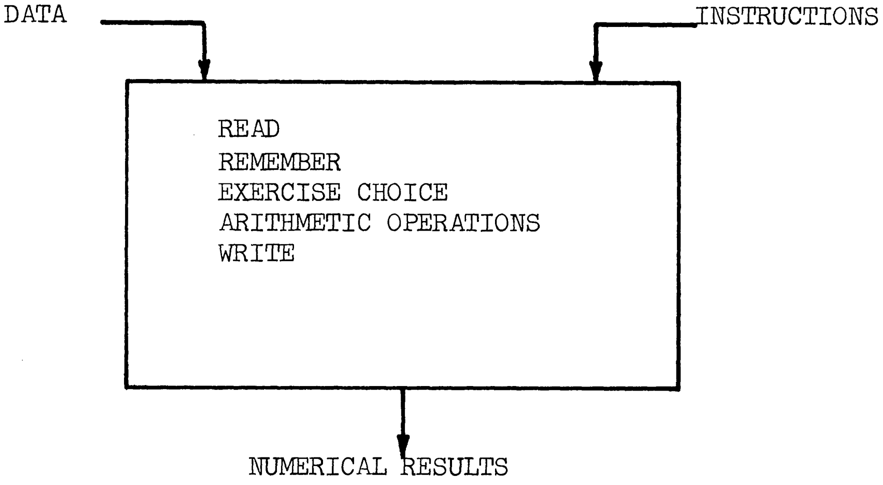

Figure XXIV-1. Digital Computer Operation.

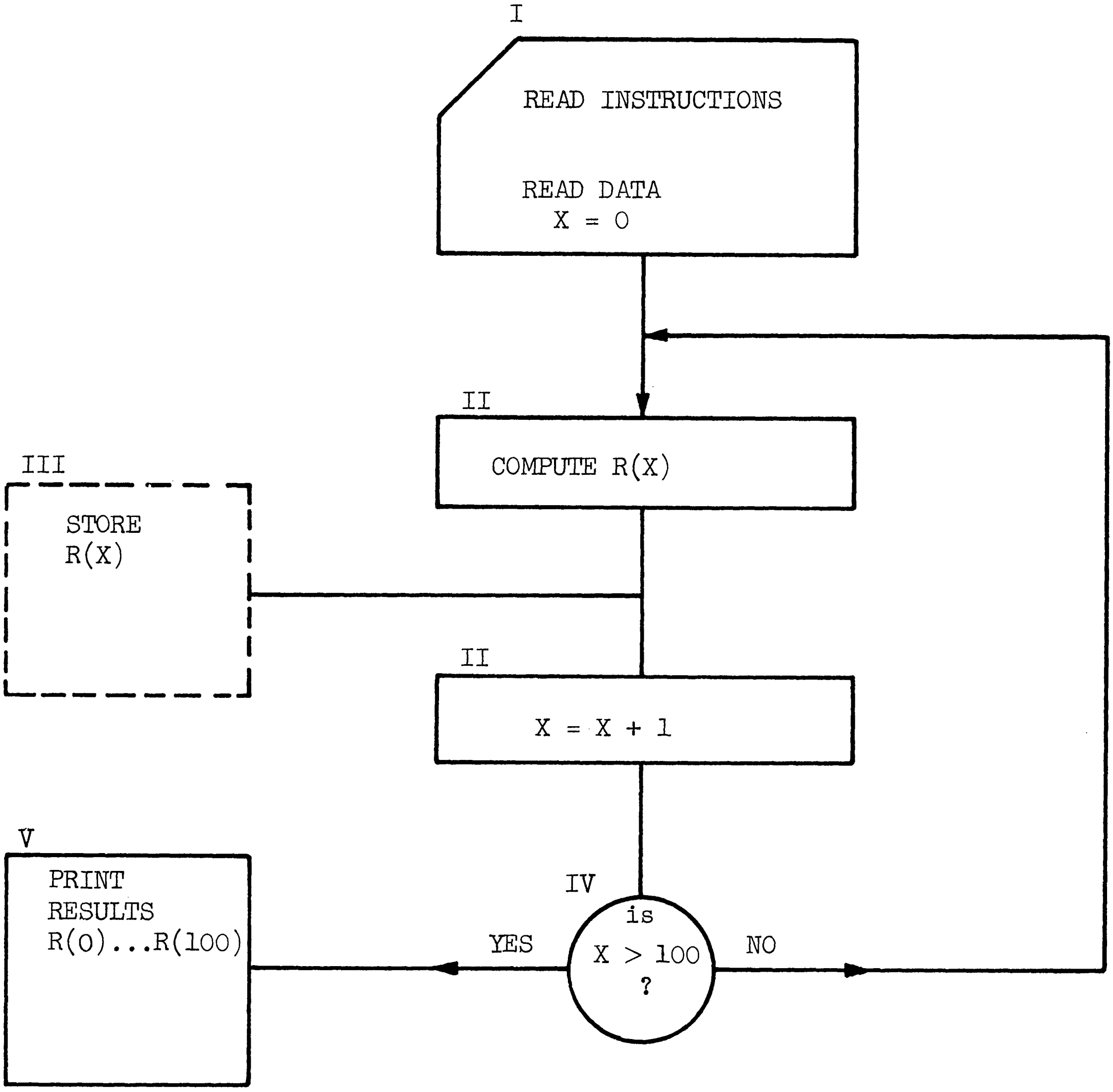

Figure XXIV-2. Flow Diagram for Successive Evaluation of Polynomial.

The overall organization of the computation is shown by a Flow Diagram in Figure XXIV-2. The instructions and initial data are read into the machine in Input Box I. The machine has been instructed to compute the result, R, for the present value of x which has been initialized at zero, Box II. The machine then stores the result, R(x), in its memory, Box III. The value of x is then incremented by one and the computer is asked to exercise choice, Box IV. If the value of x exceeds 100, the limit of the range for calculation, the computer proceeds to print the results, Box V; if not, the loop containing instructions for computation and storage, II and III is repeated, and the test at IV again imposed. When the value of x exceeds 100, the computer will call the values of R(0) . . . R(100) from memory and write them as Output V.

The flow diagram includes all of the operations which the digital computer is capable of performing, I Read, II Compute, III Remember, IV Exercise Choice, and V Write.

The Analog Computer

A particular form of the analog computer which is finding wide application in engineering is the electronic analog computer or electronic differential analyzer[2]. This device uses operational amplifiers to add, integrate, change sign, and multiply by constants greater than 1. Linear potentiometers are used to multiply by constants less than one, and servo-driven potentiometers are used to multiply. Amplifier-servo combinations are used to divide one variable by another, and the device often includes special generators to provide certain types of functions. These components are connected to provide an electrical circuit with the same mathematical description as the problem to be solved. The circuit forms a complete loop, one variable being solved for in terms of the remaining variables and then fed back into itself.

Consider an elementary example, a second-order, linear, ordinary differential equation of the form:

$$A\frac{d^2x}{dt^2} + B\frac{dx}{dt} + Cx + D = 0 \qquad \text{XXIV-2}$$

Using dot notation and solving for the highest derivative:

$$\ddot{x} = -\frac{B}{A}\dot{x} - \frac{C}{A}x - \frac{D}{A} \qquad \text{XXIV-3}$$

A flow diagram may be drawn indicating the solution to Equation(XXIV-3), as shown in Figure XXIV-3. If $\ddot{x}$ is known, $\dot{x}$ and x may be found by integration. By performing the appropriate additions and multiplications indicated by the right hand side of Equation (XXIV-3), $\ddot{x}$ is obtained and fed back into the input. This type of feedback loop is basic to solutions of equations on analog computers. The initial conditions place constraints on the voltages in the loop in order of satisfy the conditions of the problem, and the results are obtained by output voltages in the circuit.

Applications of Electronic Computers

The applications of analog and digital computers have, in general, been in keeping with the characteristics of the two types of machines[3]. The analog machine is more suited to performing dynamic simulation of processes, particularly systems which are described in terms of differential relationships with respect to time. Consequently, applications of analog computers in process design have been primarily in process simulation[4], and in the solution of problems involving rate equations[5,6,7].

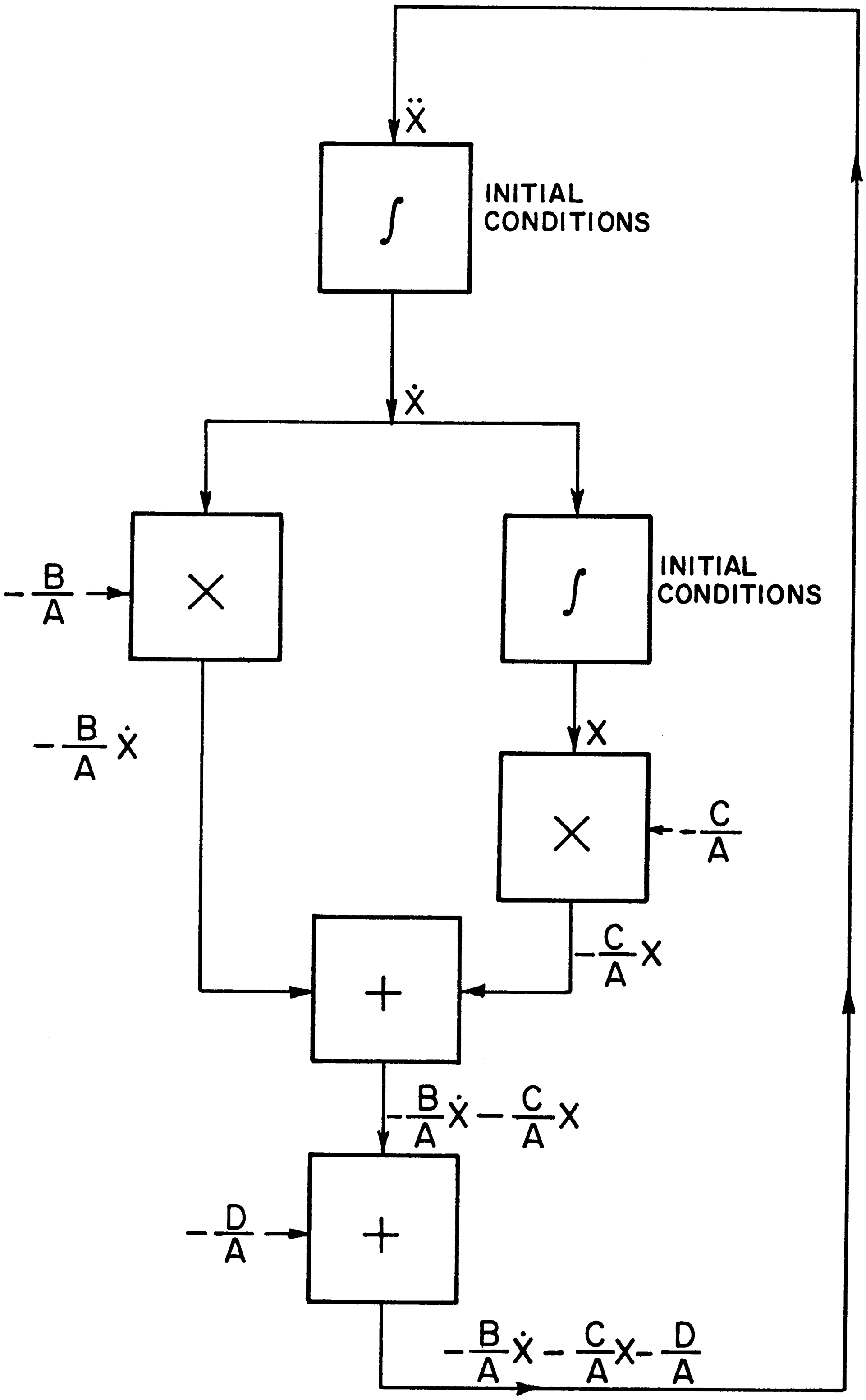

Figure XXIV-3. Flow Diagram for Solution of Differential Equation with Analog Computer.

The digital computer is more suited to algebraic or logistic problems, as well as to data reduction and processing. Applications include the solution of linear programming models (Chapter XXVl), statistical analyses, and process simulations which are too large or complex for the analog machine[8]. Several applications of a small electronic digital computer to problems in metallurgical research have recently been noted[9].

A set of 45 problems with detailed solutions by digital and analog computers has been prepared by a Ford Foundation Project at the University of Michigan[10].

Comparison of Analog and Digital Machines

The question as to whether analog or digital techniques should be employed to obtain a given problem solution often arises. The decision is not an easy one, since the advantages of one over the other may be essentially lost in practice. The decision should be based on effectiveness and cost, but other factors such as flexibility for use in other potential applications, ease of procurement, and considerations which are relative to the implementation of the machine should be weighed.

In general, the analog machine is less expensive. But whereas both computers can solve any soluble mathematical problem, the digital machine is more suitable for problems which involve logic or massive sets of data. The relative desirability of analog or digital machines for use in solving particular classes of mathematical problems has been discussed in some detail[11,12]. Table XXIV-1[13] presents a comparison of the two techniques for application to process design problems.

TABLE XXIV-1

IF you are thinking of using analog computers for process simulations-
Here are the advantages relative to digital computers...

Analog Computer	Digital Computer
Simulates behavior of any system by action of easily manipulated and measured variables	Performs arithmetic operations with numbers
Simulation is continuous, permits inclusion of concepts such as distance, velocity, acceleration	Operates discontinuously; can only approximate higher order effects
Results presented as family of graphs of variation of dependent variable (same data obtained with recorder connected to process)	Results presented as tables of numbers; must be plotted
Speed of problem solving is direct function of actual speed of physical system, is independent of size or complexity of system	Speed is direct function of problem complexity and size, relatively independent of operating speed of process
Programmed so that parameter magnitudes are entered as settings on variable potentiometers; parameter values can be changed at will	Flexibility not present without special programming precautions

BUT there are disadvantages, too .....

Analog Computer	
Size of computer (number of computing components) determines size of problem which can be solved; simplifying assumptions often made to reduce complexity	Problem size reflected in computing time; no limit to size of problem if time is available
Specifically designed for solution of ordinary differential equations; other problems--e.g., solution of simultaneous algebraic equation--made by trail and error. Less complex partial differential equations solved if converted to ordinary differential equations and one variable assumed constant; family of solutions for different values of variable results	Useful in nearly all types of problems. Complex partial differential equations more amenable to solution by digital equipment

NOW---if you think the advantages outweigh the disadvantages, here are some of the things that analog computers can do for you as compared to digital computers......

	Analog	Digital
Equipment and plant design	Show great promise for working out relative sizes of plant equipment by solving dynamic equations of plant performance	Superior for details of mechanical design--e.g., stresses, sizing of members, costs--which are trial and error arithmetical problems
Instrumentation and data reduction	Small, special purpose analogs important in converting and plotting single variable and directly correlated multiple variable data in form of graphs	
Process control Simulations (research)	Best tool in existence for studying resulting phenomenon; limitation on system complexity imposed by computer size	
Chemical plant applications	Definite promise as final control elements for units of highly automated chemical plants	Flexibility and accuracy of digital computers better for control of whole plants
Research in basic processes	Well suited to simulation of chemical reaction kinetics involved in chemical process development	Better for determination of kinetic parameters by statistical data reduction where necessary
Research in unit operations	Well suited for study of transient state such as heat transfer, distillation	Better suited for steady-state studies which are usually arithmetical or statistical
Plant operations and management technique studies		Better here because statistics and arithmetical operations predominate

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CHAPTER XXV

MATERIAL HANDLING—A QUEUEING THEORY APPROACH

Although material handling is not a unit process in the strict sense, it nevertheless plays an important role in the interrelationships of these processes. The transport of materials to and from unit processes particularly when the path is between two integrated processes plays a direct and important role in determining the overall behavior of the integrated operation. Consequently, the dynamic behavior of integrated processes is not thoroughly described without a knowledge of the handling system which takes care of the transport of materials throughout the integrated operation. The importance of material handling is born out by the fact that the rate of production of many integrated operations is truly limited by the transportation of materials to, from and within the system.

The following discussion is presented as an introduction to some of the theoretical approaches taken regarding the movement of items within a system. The presented material is not intended to be complete but only to lay a foundation for the metallurgical engineer, and outline some of the methods and procedures which are available to him when considering the design of systems which involve the transport of materials. Discussion of the types of equipment employed, the procedures and economics involved in material handling in metallurgical plants, and the design engineering of such equipment is omitted. A sound approach to plant design engineering[1] and a discussion of some of the details involved in material handling[2] are readily available in the literature. The present purpose is to encourage the metallurgical process engineer to think of a metallurgical plant, as highly complex as it may be, as a system made up of individual units, and stimulate his interest and engineering approach to metallurgical process design from the standpoint of system engineering.

Queueing Theory

Queueing theory is used to describe the mathematical approaches to problems arising whenever delays occur or priorities must be arranged regarding the sequence of a given operation. The mathematical models and solutions of the problems are the same whether the individuals or things are waiting or whether a gate is moving around to the waiting persons or objects. Applications of queueing theory have been made to a large number of problems in which waiting time is involved, including the landing of aircraft, the loading and unloading of ore ships, the design of automobile parking, waiting and traffic facilities, the passage of travelers through customs, pedestrian movements, servicing and machine breakdowns, etc.[3,4].

In the development of a queueing model one must provide for:

1. Gate or service points
2. An input process
3. Some queue discipline
4. Some service mechanism

The model then describes the situation in which customers arrive at a gate of service point, are serviced, and then leave the service area. The arrival of customers is the input process, and may be described in terms of the distribution of arrivals at the service point. As the product of the input process arrives at the service point and joins a queue, it is termed a customer. The behavior of the customer is described in terms of a queue discipline which determines how the customer reacts to the existing condition of the queue. If the queue is too long, the customer may leave the service area and be lost to the system. In the case of a multiple channel servicing system, the customer may join the queue of shortest length. Or the customer may be required to remain in the queue, irregardless of the apparent waiting time. The service mechanism is a description of the service provided in terms of the service time involved, which may be a constant or may decrease slightly with increase in queue length, or even be distributed in some manner.

The elements of interest in an analysis of the queueing problem are:

1. Waiting times for the customers
2. The number of customers in the queue
3. The ratio of waiting time to service time

The purpose of seeking a model which describes the queueing problem is to provide for the servicing of as many customers with as few facilities as possible. Generally, one optimizes the economics of the situation by seeking the minimum cost involved for some balance of waiting time between servicing unit and customer.

Single Station Queueing Problem

Let us consider the problem of determining the probability of a given queue length and the expected queue length for the case of a single station for which both input and output are assumed to be random. The queue discipline is assumed to be that each arriving unit takes the last position in the queue and that the units which make up the line are serviced in order of appearance in the line. It may be shown[5] that the probability of a waiting line of length n units, P_n, is given by:

$$P_n = (\lambda/\mu)^n(1-\lambda/\mu) \qquad \text{XXV-1}$$

if λ/μ is less than one, where λ is the mean arrival rate, and μ the mean service rate. The ratio, λ/u, is sometimes called "traffic intensity" and is the average number of arrivals per unit of service.

The mean length of a waiting line is given by the expression:

$$\bar{n} = \frac{\lambda/\mu}{[1-(\lambda/\mu)]} \qquad \text{if } \lambda/\mu \text{ is less than one.} \qquad \text{XXV-2}$$

The expected waiting time of arrivals at a single station with random input can be formulated as follows:

Let $\bar{t}_w$ = expected waiting time and $\bar{t}_s$ = expected time spent in service; then $\bar{t}_w + \bar{t}_s$ = total expected time consumed in both waiting and service. When the mean arrival rate is λ:

$$\bar{n} = \lambda\ (\bar{t}_w + \bar{t}_s), \qquad \text{XXV-3}$$

from which

$$\bar{t}_w = \bar{n}/\lambda - \bar{t}_s. \qquad \text{XXV-4}$$

It can be shown that:

$$\bar{t}_s = 1/\mu. \qquad \text{XXV-5}$$

By substitution in a previous expression, Equation (XXV-2), we obtain:

$$\bar{t}_w = [1/(\mu-\lambda)] - 1/\mu \qquad \text{XXV-6}$$

as an equation for expected waiting time at a single station.

In order that the real life situation be more closely approached by the queueing model, specific distributions for the probability of arrival have often been substituted in the model. Data taken under actual operating conditions for a sufficiently large sample have been shown to be very closely approximated by exponential or Poisson distributions in several cases.

Example of Single Station Model

Consider the case of a heat treating section consisting of a single furnace which provides service for the many areas of a manufacturing plant. The job requirements vary in a random manner as do the arrivals of parts for heat treating. The section is operated as a closed system and parts arriving remain until they are treated. It is further assumed that each job is handled in the order in which it arrives. This idealized situation corresponds very closely with the queueing model derived above.

If the mean arrival rate λ is 5 jobs per day and the mean service rate μ is 10 jobs per day, the traffic intensity $\lambda/\mu = 5/10 = \frac{1}{2}$. The probability of a waiting line of given length, n, is:

$$P_n = (\tfrac{1}{2})^n(1 - \tfrac{1}{2}) \qquad \text{XXV-7}$$

and the average number jobs waiting is:

$$\bar{n} = \frac{\frac{1}{2}}{(1 - \frac{1}{2})} = 1 \qquad \text{XXV-8}$$

If the traffic intensity λ/μ increases, the average queue length increases, becoming infinite as the service time approaches the arrival time, i.e., $(1 - \lambda/\mu) \rightarrow 0$.

The analysis above is important to the management of the manufacturing firm in determining the optimum heat treating facilities for handling a given distribution of job requests. In the simplified case above, an increase in the arrival rate to a level approaching 10 jobs per day would require that either the service times be decreased or that a multiple station arrangement be substituted, i.e., that the capacity of the facilities be increased.

Multistation Queueing Problem

Consider the case in which customers arrive at a service station and receive service from several units, S, under the assumptions made for the single station model. The probability of having to wait in line which is the sum of all probabilities that all service facilities are being used or that S or more customers are in line is given by the expression:

$$W = \sum_{n=S}^{\infty} P_n = \left(\frac{\lambda}{\mu}\right)^S \frac{Po}{S!\,(1 - \frac{\lambda}{\mu S})} \qquad \text{XXV-9}$$

where W is the probability that all service facilities are being used and P_o is the probability that zero customers are being served. The average waiting time for the case of multichannel servicing facilities is:

$$\bar{t}_w = \frac{Po}{\mu\, S(S!)\,[1-(\lambda/\mu S)\,]^2} \left(\frac{\lambda}{\mu}\right)^S \qquad \text{XXV-10}$$

and it also may be shown that the probability of no customers being served, P_o, is given by the expression:

$$P_o = \frac{1}{\sum_{n=o}^{S-1} \left(\frac{\lambda}{\mu}\right)^n / n! + \left\{ (\lambda/\mu)^S \Big/ [S!\ (1-\lambda/\mu\ S)\,] \right\}} \qquad \text{XXV-11}$$

Example of Multistation Model

The crane facilities provided in an open-hearth shop for tapping, teeming, and other pouring floor service requirements may be optimized by application of the multistation queueing model derived above.

While strictly speaking, the behavior of the handling system in a steelmaking plant does not follow the assumption of random input and output, (in fact in most plants a large staff of people are engaged in preventing it from becoming so!!!), the model permits some examination of the problem and represents a situation more extreme than normal. It may be assumed that the facilities, one, two, three, or more cranes, are the service gates which provide service to the customers (the furnaces), and do so on a basis which permits any free crane to handle the service requirements of a furnace, the furnaces queueing until service may be provided. This last assumption is also not accurate since the cranes usually operate on the same track and are not free to move around each other to change their relative position. The assumption may be justified, on the basis that a crane which has received a ladle of metal may transfer that ladle to the next crane and then proceed to provide service to a furnace further down in the shop.

Consider an open hearth shop consisting of twelve 200 ton furnaces which average 10 hours per heat. The service times for tapping, pouring, and removing the slag ladles average 1.0 hours per tap.

The average time between arrivals is 0.833 hours since in a 10 hour period, an average of 12 heats would require servicing. In a 24 hour period, an average of 28.8 arrivals would occur, requiring a total of 28.8 hours of service. This service requirement dictates that at least two cranes are necessary.

Evaluating the expected waiting times for the furnaces for two cranes may be done as follows. From Equation (XXV-11), where the traffic intensity, $\lambda/\mu = 1/0.833/1/1.0 = 1.2$ heats per average service time:

$$P_o = \frac{1}{\sum_{n=o}^{1} (1.2)^n/n! + [(1.2)^2/2![1-(1.2/_2)]]} \qquad \text{XXV-12}$$

$$= \frac{1}{(1 + 1.2) + ((1.2)^2/0.8)} = 0.250$$

$$\bar{t}_W = \frac{0.250}{(1)\ (2)\ (2)\ [1 - (1.2/_2)]^2}\ (1.2)^2 = 0.561 \qquad \text{XXV-13}$$

One may thus prepare a table indicating the waiting times for the furnaces in average service time units as shown in Table XXV-1.

The average waiting times of the furnaces are given in Table XXV-1. The total waiting time of the furnaces is given by the average waiting time per heat times the number of heats per day, 28.8. The total waiting time of the cranes is given by the available hours, 24 times the number of cranes, minus the required hours of service, 28.8.

Assuming an operating cost of $300 per hour for the furnaces and $50 per hour for the cranes, the total cost of idle time may be computed as shown in Table XXV-2. The optimum service facilities are indicated by the minimum cost and in this case are shown to be 3 cranes, a result in keeping with practice in the industry.

Other Approaches to Queueing Problems

The analytical methods presented above are relatively straightforward and the examples used to illustrate them have been greatly simplified. Only a restricted number of cases can be validly treated by these methods. There are however, techniques for determining the characteristics of a queueing system when the arrival and service distributions are not conveniently expresses mathematically. These methods are described in the literature under several headings which include:

1. Monte Carlo techniques
2. Theory of Games
3. Stochastic Processes

The problems involved in analyzing queueing situations which arise in actual integrated plant operations are extremely complex and often prohibitively difficult. However, advances are coming rapidly and

TABLE XXV-1

Summary of Calculations for Multistation Queueing Example

Arrivals per service time	Service time	No. of Cranes S	P_o	Average Furnace Waiting Time	
				Ave. Ser. Time Units	Hours
1.2	1.0	2	0.250	0.561	0.561
1.2	1.0	3	0.294	0.078	0.078
1.2	1.0	4	0.300	0.013	0.013

TABLE XXV-2

Cost Analysis for Service Facilities in Open Hearth Shop

No. of Cranes	Idle hr. Cranes	Cost of Cranes	Idle hr. Furnaces	Cost of Furnaces	Total Cost per 24 hr.
2	19.2	$960	16.2	$4860	$5820
3	43.2	2160	2.25	675	2835
4	67.2	3360	0.38	114	3474

new applications are being generated at a high rate. Consideration of these concepts is inherent to the system approach in metallurgical process design, and greater emphasis will undoubtedly be placed on the queueing theory approach to material transportation problems.

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CHAPTER XXVI

LINEAR PROGRAMMING

Linear Programming is a mathematical procedure used for solving a general class of optimization problems which involve a combination of a number of interacting factors to produce a maximum or minimum result. In order to apply linear programming, the following criteria must be met: 1) There is some function that is to be made a maximum or minimum. 2) There is a variety of solutions, each of which is subject to a set of well defined restrictions which may be expressed as equalities or inequalities. 3) Among the variables of the problem, the relationship between any two may be represented by a straight line or linear relationship at least to an acceptable degree of approximation.

The use of the linear programming model may be illustrated by the following example. Consider a metallurgical firm which wishes to produce an alloy steel of the following specifications:

Vanadium - 0.8% Minimum
Chromium - 1.8% Minimum
Manganese - 0.6% Minimum

In addition, the firm possesses a supply of two alloying materials of the following compositions:

	Alloy 1	Alloy 2
% V	40%	10%
% Cr	40%	30%
% Mn	10%	30%
% Fe	Balance	Balance

where Alloy 1 costs $4 per pound and Alloy 2 costs $2 per pound.

On the basis of the production of one hundred pounds of the desired alloy steel, let x_1 equal the number of pounds of Alloy_1 used and x_2 equal the number of pounds of Alloy_2 used.

A combination of x_1 and x_2 will produce a solution to the problem if and only if that combination satisfies the specifications for the alloy steel. This may be expressed as:

$$0.4\ x_1 + 0.1\ x_2 \geq 0.8 \qquad \text{XXVI-1}$$

$$0.4\ x_1 + 0.3\ x_2 \geq 1.8 \qquad \text{XXVI-2}$$

$$0.1\ x_1 + 0.3\ x_2 \geq 0.6 \qquad \text{XXVI-3}$$

Where: $x_1 \geq 0$ XXVI-4

$x_2 \geq 0$ XXVI-5

It is possible to show graphically the feasible solutions which satisfy the set of inequalities presented above. The shaded region of Figure XXVI-1 contains all the allowable solutions.

The solution to the problem is found in the optimum combination of alloying additions which minimize the cost function:

$$C = 4x_1 + 2x_2 \qquad \text{XXVI-6}$$

The cost function may be plotted as a family of parallel lines whose parameter is total cost. The family of parallel lines may be superimposed on the graph as shown in Figure XXVI-1 from which it may be concluded that the optimum alloying addition will occur at the vertex of the line bounded region of feasible additions. Since the firm seeks the lowest cost, the optimum alloying addition occurs at the point (0.75,5) indicating that the optimum addition consists of:

$$\left.\begin{array}{l} 3/4 \text{ lb. of Alloy 1} \\ 5 \text{ lb. of Alloy 2} \end{array}\right\} \text{ per 100 lb. of steel}$$

at a cost of: (3/4) 4 + (5) 2 = $13 /100 lb. of steel

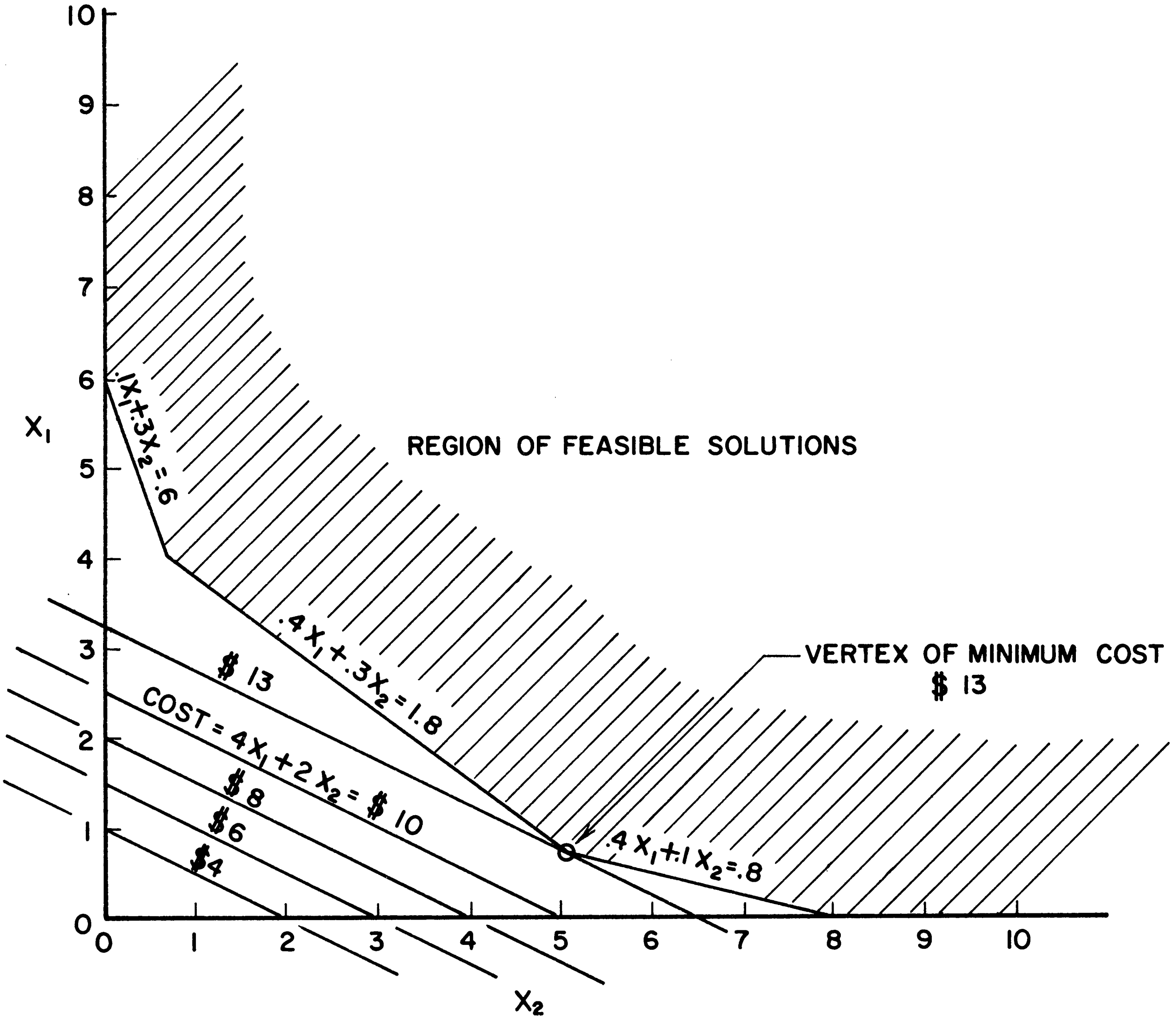

Figure XXVI-1. Graphical Solution of Two-Dimensional Linear Programming Problem.

The linear programming model in three dimensions is illustrated by the following problem. A metallurgical firm is considering the production of three high speed tool steels:

Tool Steel	%C	%M_n	% S_i	% C_r	% V	% W	% C_o
VD1	0.80	0.30	0.25	4.00	2.00	15.0	5.0
VD3	0.80	0.30	0.25	4.00	2.00	18.0	9.0
VD4	0.80	0.30	0.25	4.00	2.00	20.0	12.0

Under a government rationing plan the "critical" alloying materials tungsten and cobalt are available to the firm in the amounts of:

$$\left.\begin{array}{r}\text{1000 lb. Tungsten}\\ \text{500 lb. Cobalt}\end{array}\right\}\text{ per month}$$

The return to the company on the three products indicated above is:

VD1 - \$1.00/lb

VD3 - \$1.20/lb

VD4 - \$1.50/lb

These conditions may be summarized in the following equations:

$$0.15\,x_1 + 0.18\,x_2 + 0.2\,x_3 \leq 1000 \qquad \text{XXVI-7}$$

$$0.05\,x_1 + 0.09\,x_2 + 0.12\,x_3 \leq 500 \qquad \text{XXVI-8}$$

where x_1, x_2, and x_3 are the pounds of VD1, VD3, and VD4, to be produced, respectively. The profit function which is to be maximized is:

$$\text{Profit} = x_1 + 1.2\,x_2 + 1.5\,x_3 = \text{Max} \qquad \text{XXVI-9}$$

In this case, the region of feasible solutions is found in three dimensions and is represented by a polygon bounded by the planes corresponding to the equations above.

As in the two-dimensional case, the optimum solution will occur at a vertex of the polyhedron. In this case, the cost function will define a family of planes. It is obvious that as the number of variables increases, the geometry of this method becomes more and more complex. As a result, it is necessary to turn at this point to an algebraic approach which may be applied to any number of variables, the Simplex technique[1].

The Simplex Technique

The general maximization problem may be stated as:

$$C = \sum_{i=1}^{n} c_i x_i \qquad \text{XXVI-10}$$

where C is the function which must be maximized, subject to the restrictions:

$$\sum_{i=1}^{n} a_{ij} x_i \geq b_i \qquad \text{XXVI-11}$$

and

$$x_i \geq 0 \qquad \text{XXVI-12}$$

A parallel set of equations may be written for the general minimization problem, and it may be shown that the solution to every maximization problem is equal to the solution of the dual minimization problem, and that the converse is also true.

The problem above is phrased in the form given in Equation (XXVI-9), with the restrictions to the problem being given by Equations (XXVI-7 and -8), and:

$$x_1 \geq 0 \qquad \text{XXVI-13}$$

$$x_2 \geq 0 \qquad \text{XXVI-14}$$

$$x_3 \geq 0 \qquad \text{XXVI-15}$$

The restrictions of Equations (XXVI-13, -14, and -15) simply state that a negative quantity of high-speed steel cannot be produced, whereas those of Equations (XXVI-7 and -8) state that the amount of alloying materials used to manufacture the alloy products must not exceed the total amount available to the firm.

To proceed toward a solution by the Simplex method, the system of inequations is reduced to an equivalent system of equations by introducing new non-negative variables, x_4 and x_5, so that:

$$0.15\, x_1 + 0.18\, x_2 + 0.20\, x_3 + x_4 = 1000 \qquad \text{XXVI-16}$$

$$0.05\, x_1 + 0.09\, x_2 + 0.12\, x_3 + x_5 = 500 \qquad \text{XXVI-17}$$

These new variables, x_4 and x_5 are called "slack variables". In this problem it can be seen that the positive values of these slack variables represent the amount of alloying element which is available to the firm but which is not consumed. The profit function which is to be maximized is thus Equation (XXVI-9), the profits associated with x_4 and x_5 being zero.

The equations are now set up in the form of a matrix or table, as shown in Table XXVI-1, where the coefficients of $x_1 \ldots x_5$, i.e. the a_{ij}'s of Equation (XXVI-11), and of x_o, the b_i's of Equation (XXVI-11), are listed.

TABLE XXVI-1

x_1	x_2	x_3	x_4	x_5	x_o
0.15	0.18	0.20	1.0	0	1000
0.05	0.09	0.12	0	1.0	500

The Simplex method of calculation is based on this matrix, arranged as shown in Table XXVI-2. A column labeled "Basis" is placed to the left of the x_o column in which the basis vectors are listed, in this case, the slack vectors. A row of P_j"s are added above, where these

TABLE XXVI - 2

		P_j	1	1.2	1.5	0	0
Basis	P_{ij}	x_0	x_1	x_2	x_3	x_4	x_5
x_4	0	1000	.15	.18	.2	1	0
← x_5	0	500	.05	.09	.12	0	1
K_j	0	0	0	0	0	0	0
K_j-P_j			-1	-1.2	-1.5*	0	0

TABLE XXVI - 3

← x_4	0	166.7	.0667	.03	0	1	-1.67
→ x_3	1.5	4167	.4167	.75	1	0	8.33
K_j		6500	.625	1.125	1.5	0	12.5
K_j-P_j			-.375*	-.075	0	0	12.5

TABLE XXVI - 4

→ x_1	1	2500	1	.45	0	15	-25
x_3	1.5	3125	0	.5625	1	-6.25	18.75
K_j		7187.5	1	1.294	1.5	5.625	3.125
K_j-P_j			0	0.094	0	5.625	3.125

are the coefficients of the corresponding x_j's in Equation (XXVI-9), the profit function. A column of P_i's are added, corresponding to the P_j's but being subscripted with an i to indicate row instead of column. The profit function is then:

$$\text{Profit} = K = \sum_{j=1}^{5} P_j x_j \qquad \text{XXVI-18}$$

Next, a row of numbers, indicated by K_j, is entered where j refers to the appropriate column. The coefficients of the x_{ij}'s, the element in the ith row and jth column, are used to compute K_j as the sum:

$$K_j = \sum_i P_i x_{ij} \qquad \text{XXVI-19}$$

A row labled $K_j - P_j$ is added to the table, a value which is determined for each column.

This listing constitutes an initial feasible solution which is given by the column vector x_0 in terms of the basis vectors, x_4 and x_5.

$$x_4 = 1000 \qquad x_5 = 500 \qquad \text{XXVI-20}$$

The initial feasible solution thus consists of doing nothing, i.e., use none of the available materials, which results in a profit of K = 0.

Criteria for Optimization

The problem, once having obtained a feasible solution, is to determine whether or not a more profitable solution exists. This may be decided on the basis of the following possibilities:

A. The maximum profit is infinite and has been obtained by the present program. This is true if all x_{ij} are less than or equal to zero in a column where $K_j - P_j$ is negative.

B. The maximum profit is finite and has been obtained by means of the present program. This condition may be recognized when all $K_j - P_j$ are positive or zero.

C. An optimal program has not yet been found, i.e., larger values of K exist. This case requires further calculation and is identified if some x_{ij} are positive when $K_j - P_j$ is negative.

Procedure for Calculation

When situation C exists, choose the most negative $K_j - P_j$. In the present example, this is $K_3 - P_3 = 1.5$, as indicated by the asterisk in Table XXVI-2. This determines which of the x_j's will be entered into the Basis column in Table XXVI-3. To determine which vector will be replaced, divide each of the positive x_{ij}'s appearing in the selected column into the corresponding x_{i0} which appears in the same row under x_0. The smallest of these ratios then determines the vector to be replaced. In the present example, the ratios $x_{10}/x_{13} = 1000/0.2$ and $x_{20}/x_{23} = 500/0.12$ are considered, the second being the smaller and indicating that the second row, vector x_5 is the one to be replaced. This is indicated by the arrow in Table XXVI-2, and a new basis is formed consisting of x_4 and x_3.

The elements of the row to be entered are calculated by dividing each element of the row being removed by the element in the selected column. Thus as shown in Table XXVI-3, x_3, the row corresponding to x_5, has been formed by dividing each element of x_5 by x_{23} of Table XXVI-2, 0.12 in the present case.

The remainder of the table is formed in the following manner. Select a constant which when multiplied by the element of the row to be removed in the selected column gives the negative of the element in another row of that same column. Multiply each element of the row to be removed by that same constant and add the element to the element in the other row. Repeat this procedure until all rows have been thus modified, the result being that the selected column will consist of zeroes except for a one in the row which was entered as shown in Table XXVI-3 for column x_3. In the problem under consideration, each element in row 2 of Table XXVI-2 was multiplied by -1.667 and added to the corresponding element in row 1, thus generating row 1 of Table XXVI-3. In the general case, this procedure would be carried out for all of the several rows which might be present.

The K_j's are then computed by Equation XXVI-19, and the values of $K_j - P_j$ determined. The procedure is then repeated until either situation A or B exists. In the present case, the solution is obtained after two iterations. The optimal solution is presented in terms of the pounds of alloys produced, pounds of materials used, and the profits in Table XXVI-5.

The example selected has been intentionally simple in order to present the basic procedures involved in the Simplex technique. In general, applications of the linear programming model involve very high order matrices which are treated by the iterative procedure indicated above. Such a situation immediately brings to mind the use of a large scale digital computer. And in fact, digital computers have been used to great advantage in the solution of several linear programming problems.

TABLE XXVI-5

Optimum Program for Alloy Production

Alloy	lb. produced	lb. W	lb Co	Profit
VD1	2500	375	125	$2500.00
VD3	0	0	0	0
VD4	3125	625	375	4687.50
Total		1000	500	$7187.50

This table indicates that the optimum profit is obtained when only alloys VD1 and VD4 are produced in the amounts of 2500 and 3125 lb., respectively. The entire allotment of tungsten and cobalt is used in the production of these two alloys, to the exclusion of alloy VD3.

Applications of Linear Programming

Linear programming has found considerable application in the field of business planning and operation. Problems which have been solved by linear programming techniques include personnel assignments, the blending of aviation gases[5], contract awards[6], allocation of manufactured products[7,8], and the long-range planning of coke-oven replacements[9], as a few examples.

The use of linear programming for control of technical processes has been developing rapidly in all fields of science, particularly in the chemical industries[10, 11, 12]. Fabian[13] has proposed the use of linear programming to determine the least cost rate of input of materials into an integrated steel mill. Although Fabian's treatment of the problem is relatively limited, it clearly illustrates the potential of the method and represents an excellent approach to a very difficult problem. Hilty et.al.[14] have used linear programming to predict the minimum materials cost for stainless steels.

It should be noted that the foregoing discussion is by no means complete. In addition to the Simplex technique which was introduced in this chapter, a very powerful and simple approach to the problem termed the transportation technique is desirable for use whenever possible for large-scale problems since it involves the simplest arithmetic operations. The transportation technique will not, however, handle the general class of linear optimization problems as will the Simplex technique[15]. The use of linear programming, particularly in conjunction with large-scale digital computers, should offer an excellent means of utilizing the vast amount of fundamental data that is being produced in various areas of process metallurgical engineering. By combining these data with the available operating and economic data in the form of linear programming models, many problems both economic and operative which face the metallurgical process engineer may be greatly clarified and suitable solutions worked out using this technique.

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CHAPTER XXVII

Process Simulation

One of the principal applications of computers to process metallurgical engineering is in the area of process simulation. A detailed computer simulation of a process to determine the effect of all process parameters on yields and on by-product formation requires the derivation of a complete reaction model. An accurate simulation of a process permits optimum processing conditions to be specified before any final plant design or plant tests are made, thereby eliminating many of the difficulties of scale-up and the requirement of pilot plant tests.

The derivation of an accurate dynamic model is often not an easy task, and one is faced with the alternatives outlined in Chapter V:

1. A description of the dynamics of the process in terms of a series of differential equations which describe the mass and energy transfer processes which occur in the reactor.
2. A description of the process dynamics in terms of the operating results of similar reactors which are already in commercial use. A detailed description of the change in chemical concentrations, temperatures, flow rates, etc., as functions of time may be reduced to descriptive functions by numerical analysis with the assistance of a digital computer, or by trial and error techniques using an analog computer.
3. The system may be described in terms of the average operating characteristics for the particular type of reactor

based on the observations made on commercial-sized units. The particular reactor may present a characteristic concentration-time relationship, or may involve temperature dependences which are easily observable. In this case, the average operating results may be applied to the system which is in the design stage. This model is not entirely a dynamic one, but is certainly highly descriptive of the process and may be used to some advantage.

4. In the case of metallurgical reactors in which the mechanisms of the processes being carried out are not at all understood, one may neglect the process dynamics and select a process time for a batch unit or a suitable flow rate for a continuous unit on the basis of either previous experience or good engineering judgement. Although this final choice is far from a satisfactory one, the reduction of the process model to a mass and energy balance does permit the evaluation of many of the process variables and furnishes a basis on which the dynamics of the process may be either estimated or evaluated after construction of the pilot plant or commercial-sized unit.

The set of simultaneous equations describing the process system includes one for each separate chemical species formed or utilized in the chemical reactions comprising the process. The mass and energy balances for each chemical species are interrelated in the form:

$$\frac{dQ}{dt} = -V \frac{dC}{dt} \Delta H \qquad \text{XXVII-1}$$

where V is a factor which converts concentration to weight units, C is the concentration of the product, ΔH is the change in thermal energy during the reaction for each weight unit formed, and $\frac{dQ}{dt}$ is the rate of heat gain to the complete reactor system. As outlined in Chapter II, heat transfer equations may then be set up to include:

1. The energy manifested as a temperature change in the reaction mass.
2. The energy representing that appearing as a temperature change in the reaction vessel.
3. The energy transferred to or from the surroundings.

Having expressed the process variables in such a set of simultaneous differential equations, the dynamics of the system may be included in the process model in the form of a differential equation involving the changes in concentration with respect to time as functions of process geometry and chemical driving forces.

Consider for example the reaction which takes place when a reactive gas is contacted with a liquid metal. The differential equation describing the solution of gas in liquid metal has been presented in Chapter IV and may be expressed as:

$$\frac{dc}{dt} = \frac{D}{\delta}\,\frac{A}{V}\,(c_e - c) \qquad \text{XXVII-2}$$

If the particular gas under consideration is nitrogen, and the melt is pure liquid iron, the mass and heat balances may be interrelated by the relationship:

$$\frac{dQ}{dt} = -\left[\frac{dc}{dt}\right]\frac{W}{100}\quad\frac{860}{14} \qquad \text{XXVII-3}$$

where: $\frac{dQ}{dt}$ is energy transferred to the system in cal/sec, $\frac{dc}{dt}$ is the rate of change of concentration in wt. %/sec, W is the weight of the melt in grams, (860/14) is the heat of solution in cal/gm.

The dynamics of the process may then be expressed in terms of equations XXVII-2 and XXVII-3. These equations, when coupled with the mass and energy balances may then form a process model suitable for simulation. The dynamics of this simple process are very well understood, and the computer simulation of such a process would yield highly accurate results. This particular model would correspond to the dynamic process, Model 1 indicated above.

Process model 2 would involve the observation of the behavior of the system with respect to mass changes; that is, gas going into solution in the metal and temperature changes along with the variation in those quantities entering into the mass and energy balances. Such data could then be reduced on a computer to a dynamic model which would yield a highly accurate simulation of the process, accuracy of course, depending upon the reliability and extensiveness of the data taken. Process model 3 would involve the averaging of data observed on many systems involving gas-metal equilibria, and the application of such generalized gas-metal behavior to the system under consideration. One might assume, for example, that the gas content of the metal varies linearly with time and that the average time of solution is given by a certain number of minutes. Such a model, of course, is not highly accurate, but does permit a reasonable prediction of the behavior of such a gas-metal equilibration process.

The final dynamic model, which was essentially to ignore the variations in process variables with respect to time and merely examine the overall results, can also be applied to this particular process. If the equilibrium state of the system is known, and one has reason to believe that sufficient time will be allowed to approach this equilibrium condition, the mass and energy balances of the system may be written on this basis.

The example system selected above was a highly simplified one. In the general case, there are a large number of concentration variables as well as many ill-defined thermal and geometrical parameters involved. In most metallurgical process operations, one is faced with the relatively difficult task of not only evaluating each of these variables, but also attempting to write a descriptive model which involves their interactions as well. Much of this data has become available in the last few years and considerable work is presently being expended in this direction. It is thus expected that approach 1 will become more and more important as metallurgical process operations are better understood. In the present situation, the availability of high-speed computing equipment as well as the installation of better instrumentation and control systems in metallurgical plants should permit very advantageous use to be made of approach 2. The development of data processing techniques and the success with which simulation of processes has been used, particularly in the chemical industries, should be an indication to the practicing metallurgist that considerable clarification may be brought to bear on the operation of metallurgical processing plants.

In attempting to write descriptive models for the purpose of process simulation, one should bear in mind some of the basic elements of process dynamics. It may be noted that the dynamic behavior of a chemical process depends upon the kinetics of the reactions involved, upon the manner in which the environment variables change with time, and upon the geometry of the system. To relate these factors quantitatively requires that differential equations be formed to express the interrelation which exists between physical variables. As indicated above, these data are generally not available; or if available, are not easily solved by means of arithmetical methods because they are non-linear equations. However, it is often unnecessary to make a precise study of the dynamics of the process in order to sufficiently approximate the reactor dynamics to a degree that may be useful in obtaining engineering results.

The rates of metallurgical reactions may range from very slow to very rapid. The relative speed of the reaction with respect to the residence time in the system determines whether the chemical reaction process or the material handling process has the dominant role in the process kinetics. When mixing lags are small and reaction rates are slow, the dynamic behavior of the system may be determined largely by the chemical kinetics.

However, when reaction rates are high and material handling lags large, the situation reverses. Instantaneous conversion of charge material into product can be assumed and the kinetics of the process treated on the basis of the material handling dynamics of the product emerging from the system. If material handling is the rate controlling step, static material balance equations may be used to describe the conversion of raw material into product in an "ideal system". These equations can be then modified by the appropriate functions to describe mixing and transportation of material.

In addition to the above concepts, a number of assumptions are often made to facilitate the formulation of a descriptive process mode. Batch and continuous stirred systems are generally considered to be perfectly mixed, that is, there are no temperature or concentration gradients existing in the reacting materials. The heat transfer coefficients throughout the system are considered to be constant at the ambient operating temperatures of the system. The heat transfer coefficients used, although assumed constant, would be characteristic of the particular media involved. That is, the heat transfer coefficient between the charged material and the reactor walls and the heat transfer coefficient between the system walls and the surrounding are assumed to be constant although most probably of a different magnitude. The temperatures within the system are assumed to be constant although possibly different in different areas, or different media within the system. The use of these assumptions of course involves their justification in the application for which they are used, and in this regard, one must often rely on engineering judgement, particularly in the case where previous experience in the area is not available.

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CHAPTER XXVIII

SYSTEM ENGINEERING

The goal of this text to the present point has been to provide a basic understanding and an engineering approach to the unit processes involved in metallurgical process engineering. This is the foundation of metallurgical process engineering. But, as a goal itself, it is inadequate. In recent years, the processing industries have come to realize more and more that they may no longer think of their plants as an assemblage of unit processes interconnected by material handling and mass transport systems. The individual components of a metallurgical plant should not be designed for a specific operation in view of the fact that each of the separate units in such a plant influences the others in subtle as well as direct ways. In the face of such a situation, the engineer is forced to view the metallurgical plant and each of its component unit processes as an integrated system. The system viewpoint or approach to engineering design is rapidly being demonstrated to be vastly superior to an approach which evaluates each unit process on its own merits and then attempts to connect the several "best" processes into an integrated operation. It is also becoming apparent that control instruments need to be specified with the process as a whole in mind rather than merely the specific processing unit alone on which the instruments are to be installed.

System engineering may be defined in terms of the engineering approach to plant and process design which it involves:

1. Consideration is made of all aspects of the design of the proposed plant as a single unit including kinetics, heat and

mass balances, and process dynamics as well as instrumentation and automatic control.

2. Recognition is made of the fact that the relationships which are involved in such a comprehensive approach may be numerous and complex and with this in mind the use of electronic computers, both analog and digital, is given full consideration.
3. The assistance of basic and applied research organizations are sought to provide the greater amounts of basic data which are necessary for such an approach to design of process operations.
4. The inclusion of automatic control concepts in the integrated system design is considered to be almost a necessity in order to provide optimum operation of the system as a whole.

Any processing system for the handling of chemical or mineral raw materials may be described as a network of alternating reaction and separation zones. Raw materials and energy are supplied to a reactor from which flows the product in the form of a mixture of desirable and undesirable materials. The products leaving the reaction zone are usually hot and must be cooled down before they can enter succeeding operations. From the product stream, energy is extracted. This operation may occur before or after the separation operation in which the desired products are removed from the product stream of the reactor. In view of these considerations, the system engineer would favor reaction systems which provide a means for exchanging energy between the cooling down of the product stream and the heating up of the input feed stream. Certain types of metallurgical process systems possess distinct advantages on this basis alone.

In addition to the specific reaction vessels which make up the system, the process metallurgical engineer must consider waste removal and material handling problems, and should evaluate the reactor type and the particular components of the system as part of an orderly system design study. One must also consider factors which are exterior to the system design. Such problems would include the choice of raw materials and the ability of the system to handle the wide variation in raw material properties, which the feed might possess. Waste disposal problems are also a factor which must be considered with the view of the entire system in mind. Economic factors such as depreciation procedures, tax situations, public relations, and other forces which bear upon the business decisions the management of the firm may make must also become an integral part of the system design.

In order to accomplish this large and formidable task of providing an adequate system design, the process metallurgical engineer will be required to draw upon basic scientific information relating to the process under consideration, to the use of analog and digital computers, as well as to the use of advanced mathematical techniques in order to evaluate and describe the numerous and complex relationships which exist between the components of a system. The engineer must be well founded or at least familiar to the point that he is able to make use of the rapidly-developing techniques of operations research in order that he might provide for an orderly flow of materials, equipment, and labor to produce the maximum product at the minimum cost. Having developed relationships regarding the influence of the components of the system on one another, the system engineer may provide an adequate description of the system in terms of the integrated models for each of its components. The techniques of linear programming will be of considerable advantage in seeking the solution to such a problem.

System engineering is a rapidly developing and highly advanced approach to process design. It is expected that in the future by system procedures, processes may be designed from fundamental kinetic data with the design yielding specifications for optimum operating conditions. Based of course on the accuracy of the models derived, it is expected that economic evaluations can be made with confidence, and cost may be predicted more accurately than at the present time. If proved, system design based on a knowledge of process dynamics can trim down the design of particular units and yield a less expensive but improved system which is able to operate at optimum conditions under the guidance of improved control systems. Capital investment could then be reduced and maximum production obtained from any given equipment with improved quality as a result of improved control. Computer simulation of processes has been demonstrated to be feasible and to be economically advantageous. Research into process system behavior and the mathematical representation thereof have resulted in improved control systems, as for example, in the petroleum industry's computer controlled plants.

The process metallurgical engineer is presently placed in a position which requires that he be familiar with the techniques of system engineering, for just as it is possible to design and build a computer controlled plant with highly complex but very effective control, it is just as easy to design a system involving extensive and costly control systems which are computer oriented but are not economically justifiable. The computer might be over-taxed as a control element and essentially become an expensive data recorder, or be required to carry out duties which could be just as easily handled by much simpler and cheaper standard controllers. The metallurgical process engineer engaged in such system design has a great responsibility in seeing that proper installations are specified.

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INDEX

INDEX

Index

Index

Index

Index

Index

Index

TABLE OF PHYSICO-CHEMICAL CONSTANTS

Acceleration of gravity, standard	32.17 ft. sec^{-2}
Atmosphere, standard	760 mm Hg
	14.7 psi
Avogadro's number, N	6.02 x 10^{23} mole^{-1}
Boltzmann constant, R/N, k	1.38 x 10^{-16} erg degree^{-1}
British Thermal Unit	252 g-calories
	778 ft-lb
Calorie, gram	4.183 int joules
Coulomb	1 ampere-sec
Electronic charge, e	4.80 x 10^{-10} esu
	1.6 x 10^{-19} abs coulomb
Electronic Mass, M	9.106 x 10^{-28} gram
Faraday, F	96,496 abs coulomb equiv^{-1}
	23,060 cal volt^{-1} equiv^{-1}
Gas constant, R	0.730 cu ft-atm °R^{-1} lb.-mole^{-1}
	1.987 cal °K^{-1}g-mole^{-1}
	8.314 x 10^{7} erg °K^{-1} g-mole^{-1}
Horsepower, 1 hp	33,000 ft-lb min^{-1}
Ice point, 0°C	273.16 °K
32°F.	491.7 °R
Kilowatt, kw	1.341 hp
Neutron mass	1.6745 x 10^{-24} gram
Planck's constant, h	6.62 x 10^{-27} erg sec.
Protron mass	1.6723 x 10^{-24} gram
Stefan-Boltzmann constant, σ	5.672 x 10^{-5} erg cm^{-2} sec^{-1} degree^{-4}
	0.173 x 10^{-8} Btu ft^{-2} hr^{-1} °R^{-4}
Velocity of Light in Vacuum	2.998 x 10^{10} m sec^{-1}
Volume of ideal gas, STP	22.414 liter g-mole^{-1}
	359 cu ft lb-mole^{-1}