# THERMODYNAMIC PROPERTIES OF URANIUM–BISMUTH ALLOYS*

### A. COSGAREA, Jr.,† E. E. HUCKE‡ and D. V. RAGONE‡

Thermodynamic properties of uranium–bismuth alloys were determined by measuring the vapor pressure of bismuth in equilibrium with the condensed phase. Classical methods based on the rate of sublimation, rate of evaporation or rate of effusion could not be used since each method requires an accurate knowledge of the molecular weight of the vapor. The molecular weight of bismuth is not accurately known, but the presence of Bi and $Bi_2$ species has been established.

An optical absorption technique was used to determine the concentration of each species independently. Briefly, this method consists of measuring concentrations in a vapor by the quantity of light absorbed at certain characteristic frequencies by the species in the vapor. The amount of each species present, which is related to the pressure, was determined by measuring the diminution of intensity at 3067 and 2731 Å. The amount of radiation absorbed was found to be dependent on the thickness of the vapor space and the concentration of the bismuth vapor.

The thermodynamic activity of bismuth was measured at temperatures from 725 to 875°C in the regions: $U_3Bi_4$ + $UBi_2$, $UBi_2$ + liquid and the one-phase, liquid region. In order to obtain measurable quantities in the regions UBi + U and UBi + $U_3Bi_4$ it was necessary to work at temperatures from 800 to 1000°C. From a measure of the activity of bismuth, the activity of uranium was calculated for the entire system. The liquid uranium–bismuth alloys were found not to be regular solutions. The Henry's law parameter ($3.49 \times 10^{-3}$ at 1064°K) was found to be valid for uranium concentrations of less than 2 mole % uranium. From a complete knowledge of the activities of uranium and bismuth in the system the partial molar quantities and integral molar quantities were calculated at five temperatures: 1018, 1041, 1064, 1089 and 1115°K.

## PROPRIETES THERMODYNAMIQUES D'ALLIAGES URANIUM–BISMUTH

Les propriétés thermodynamiques d'alliages uranium–bismuth ont été déterminées par la mesure de la pression de vapeur de bismut en équilibre avec la phase condensée. Des méthodes classiques basées sur la vitesse de sublimation, la vitesse d'évaporation ou la vitesse de dégagement ne pouvaient pas être employées puisque chaque méthode nécessite une connaissance exacte du poids moléculaire de la vapeur. Le poids moléculaire du bismuth n'est pas exactement connu mais la présence des espèces Bi et $Bi_2$ a été établie.

Une technique d'absorption optique a été employée pour déterminer la concentration de chaque espèce indépendamment. Cette méthode consiste brièvement à mesurer les concentrations dans un gaz par la quantité de lumière absorbée par les espèces dans le baz à des fréquences caractéristiques déterminées. La quantité de chaque espèce présente, qui dépend de la pression, était déterminée en mesurant la diminution de l'intensité à 3067 et 2731 Å. On a trouvé que la partie du rayonnement absorbé dépendait de l'épaisseur de l'espace gazeux et de la concentration de la vapeur de bismuth.

L'activité thermodynamique du bismuth a été mesurée pour des températures de 725–875°C dans les régions: $U_3Bi_4$ + $UBi_2$, $UBi_2$ + liquide et dans la phase liquide. Pour obtenir des quantités mesurables dans les régions UBi + U et UBi + $U_3Bi_4$, il était nécessaire de traailler à des températures entre 800 et 1000°C. L'activité de l'uranium fut calculée pour tout le système à partir d'une mesure d'activité du bismuth. On a trouvé que les alliages liquides d'uranium–bismuth ne sont pas des solutions régulières. Le Le paramètre d'après la loi de Henry ($3,49.10^{-3}$ à 1064°K) a été trouvé valable pour des concentrations d'uranium de moins de 2% molaire d'uranium. A partir d'une connaissance complète des activités d'uranium et de bismuth dans le système, les quantités partielles molaires et les quantités molaires intégrales ont été calculées pour cinq températures: 1018, 1041, 1064, 1089 et 1115°K.

## THERMODYNAMISCHE EIGENSCHAFTEN VON URAN–WISMUT-LEGIERUNGEN

Die thermodynamischen Eigenschaften von Uran–Wismut-Legierungen wurden aus Messungen des Gleichgewichtsdampfdrucks von Wismut über der kondensierten Phase ermittelt. Klassische Methoden, die auf der Geschwindigkeit der Sublimation, Verdampfung oder Effusion beruhen, ließen sich nicht anwenden, da für jede dieser Methoden eine genaue Kenntnis des Molekulargewichts des Dampfes erforderlich ist. Das Molekulargewicht von Wismut ist nicht genau bekannt, doch wurde das Auftreten einer Bi- und einer $Bi_2$-Art festgestellt.

Die Konzentrationen der beiden Arten wurden einzeln mit einer optischen Absorptionstechnik bestimmt. Die Konzentration in einem Dampf wird dabei gemessen durch die Lichtmenge, die bei bestimmten charakteristischen Frequenzen von den verschiedenen Arten im Dampf absorbiert wird. Der Anteil von jeder vorhandenen Art, der vom Druck abhängt, wurde durch die Intensitätsschwächung bei 3067 und 2731 Å bestimmt. Der Betrag der absorbierten Strahlung ergab sich als abhängig von der Dicke des Dampfraumes und der Konzentration des Wismutdampfes.

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Die thermodynamische Aktivität Wismuts wurde bei Temperaturen von 725 bis 875°C gemessen in den Zustandsgebieten $U_3Bi_4$ + $UBi_2$, $UBi_2$ + Schmelze und in der einphasigen Schmelze. Um meßbare Ergebnisse in den Gebieten UBi + U und UBi + $U_3Bi_4$ zu erhalten, war es notwendig, bei Temperaturen zeischen 800 und 1000°C zu arbeiten. Aus der Messung der Wismut-Aktivität wurde die Aktivität des Urans für das ganze System berechnet. Es wurde gefunden, daß die flüssigen Uran–Wismut-Legierungen keine regulären Lösungen sind. Der Parameter des Henryschen Gesetzes (3,49 × 10⁻³ bei 1064°K) ergab sich als gültig für Urankonzentrationen kleiner als 2 Mol% Uran. Aus der vollständigen Kenntnis der Aktivitäten von Uran und Wismut in diesem System wurden die partiellen und integralen molaren Größen für fünf Temperaturen: 1018, 1041, 1064, 1089 und 1115°K berechnet.

## INTRODUCTION

The fugacity of a constituent in a liquid or solid mixture may be determined by measuring the fugacity of that constituent in the vapor in equilibrium with the condensed phase. The activity of the constituent in an alloy, $a_i$, is the ratio of the fugacity in that state, $f_i$, to the fugacity of a standard state, $f_i^0$,

$$a_i = f_i/f_i^0.$$

Under the conditions of high temperature and low total pressure, pressure is very nearly equal to fugacity.

Hence:

$$a_i = \frac{f_i}{f_i^0} = \frac{p_i}{p_i^0}.$$

Note that it is not essential that absolute pressures be measured. A measure of a relative pressure, $Ap$, would also provide thermodynamic activity measurements,

$$a_i = \frac{p_i}{p_i^0} = \frac{Ap_i}{Ap_i^0}.$$

Several factors must be taken into consideration in selecting a technique for measuring the vapor pressure of bismuth in equilibrium with uranium–bismuth alloys. First, the alloys of uranium–bismuth are pyrophoric and quite reactive in the liquid and solid state. Secondly, and most important, the molecular weight of bismuth vapor is not accurately known.

It is not possible to use the rate of sublimation, rate of evaporation and rate of effusion techniques unless a complete knowledge of the vapor pressure species of bismuth is known. The use of a e.m.f. cell for measurement of thermodynamic activities in the uranium–bismuth system at high temperature is also prohibited from a container standpoint.

When the molecular weight of the vapor is not known accurately, an optical absorption technique can be used to determine the concentration of each species independently. Briefly, this method consists of measuring concentrations in a vapor by the quantity of light absorbed at certain characteristics frequencies by the species in the vapor. This method has been used to measure thermodynamic activity in some monatomic vapors. Hirst and Olsen[1] measured the vapor

pressure of mercury above amalgams. Herbenar et al.[2] have applied the method to measure relative vapor pressures of zinc over copper–zinc alloys. The optical absorption technique is even more powerful in determining vapor pressure in systems in which the volatile constituent has more than one molecular form in the vapor. This technique has been used in this study for measurement of thermodynamic activity in the uranium–bismuth system.

## THEORY OF ABSORPTION MEASUREMENTS

Atoms and molecules are able to radiate or absorb light of definite frequencies which are determined by the characteristic energy states of the constituent. In order to perform measurements of the vapor pressure of bismuth, it is necessary that the two species of bismuth vapor be distinguishable. This can be done by selecting proper energy transitions in the absorption spectrum of bismuth.

Monatomic bismuth is detected by observing the absorption of radiation at a discrete wavelength by ground-state electrons in the free atom. The radiation absorbed from the collimated beam at 3067 Å raises the electron from the 6-$p$ level to 7-$s$ level. The duration of the energy transition is estimated to be of the order $10^{-7}$–$10^{-9}$ sec. When the electron returns to the ground state it emits its resonance radiation in a random direction. The 3067-line transition for atomic bismuth was used for a measure of the number of bismuth atoms in the vapor. Since this energy transition is one from the ground state to a higher energy it will give a measure of the bismuth monatomic vapor pressure. The amount of bismuth atomic pressure will be related to the diminution of intensity at the wavelength 3067 Å.

Diatomic bismuth exhibits a complex band system composed of individual electronic bands, each accompanied by its own vibrational and rotational lines. In the same manner as for the atomic constituent, the diatomic population is measured by observing the absorption of energy at a discrete wavelength. For diatomic bismuth the electronic band head at 2731 Å has been used to represent a molecular energy transition from the ground state to an excited state.

The amount of radiation absorbed at frequencies 2731 and 3067 Å is dependent on the thickness of vapor space and the concentration of the bismuth vapor. This correlation can be expressed by the Beer–Lambert law:

$$\ln \frac{I_x}{I_0} = -\mu c x$$

where $I_0$ = intensity of incoming radiation of a certain frequency

$I_x$ = intensity out of the cell,

$\mu$ = extinction coefficient,

$x$ = length of the optical path through the cell and

$c$ = concentration of specie in vapor.

Since $c = N/V$ and the gas is ideal, $c = p/RT$ and

$$\ln \frac{I_x}{I_0} = -\mu x \frac{p}{RT}.$$

Thus, a measure of the logarithmic intensity decrease at any given temperature yields the pressure multiplied by a constant. This constant, $\mu x/R$, is a function of the variables of the equipment and the vapor species.

Representative absorption line transitions and band absorption transitions for bismuth vapors at four temperatures are shown in Fig. 1. The bismuth resonance line at 3067 Å is shown at the left, and the band head at 2731 Å at the right. The transitions were recorded by transversing from right to left (increasing wavelength). It is to be noted that the absorption line transition is not perfectly monochromatic, but has some broadening due to the limited resolution of the spectrograph, natural line broadening due to the finite life-time of the excited state, and the Doppler-effect broadening due to the motion of the atoms. However, a constant ratio of peak height to line width was observed over the temperature range employed. Over the same temperature range the band structure was also observed to remain constant.

### APPARATUS

A schematic diagram of the apparatus used is shown in Fig. 2. The light source used to supply a continuum in the desired frequency range was a high pressure mercury lamp manufactured by General Electric, H85-C3. The lamp was contained in a water-cooled jacket and the power input to the lamp was stabilized by a voltage regulator. The intensity of light output from the lamp can be controlled to no more than 1 per cent fluctuation in intensity output. The lamp emits an approximately continuous intensity over the wavelength region from 2600 to approximately 4000 Å.

However, the intensity of the source is greater in the vicinity of the mercury emission lines. The lamp yields sufficient radiation at wavelengths, 3067 and 2731 Å, to provide the necessary energy source for bismuth vapor excitation.

The cell used for bismuth vapor measurement and measurements of bismuth vapor pressure over uranium–bismuth alloys is shown in Fig. 3. The cell was made entirely of quartz with optically-flat, polished windows. Quartz cells were procured with varying window space distance from the Euclid Glass Engineering Laboratory, Cleveland, Ohio. The spaces employed were from 1 to 50 mm.

The furnace used to heat the quartz cell is a split-wound resistance type furnace. The furnace has two main windings which heat the general surface area of the furnace. Two end windings, separately controlled, are also employed to offset the effect of end-cooling. By means of regulating the power input to the various windings, it was possible to control the temperature in the immediate vicinity of the cell to ± 1°C. The necessary isothermal volume in the furnace is a cylinder 2 in. in diameter and 4 in. in length. A boat containing the bismuth or uranium–bismuth alloy and the windows were located in the center of this isothermal range. Temperatures were measured in four different positions along the cylinder by means of calibrated chromel–alumel thermocouples. The thermocouples were placed in the immediate vicinity of the cell.

Since it is necessary to have a parallel beam of light going through the absorption cell, a lens system must be used to condense the divergent rays from the mercury light source. A plano-convex lens was placed at its focal distance from the mercury lamp source in order to give a parallel beam of light through the absorption cell. After passage through the cell the light was condensed by means of another plano-convex lens before it reached the spectrograph. This was necessary because the mercury lamp source was not a point source and hence some divergence was still present. This did not affect the measurements, however, since the path length through the cell was less than 5 cm. In this length the beam of light was essentially parallel.

The absorbed radiation was analysed by means of a Leeds and Northrup spectrochemical analyser. The unit contains a small plane grating monochromator. The spectrometer is 30 in. long and uses a 3-in. wide grating with 30,000 lines per inch. Spectra have been obtained which demonstrate a second-order resolution of 0.05 Å in the visible and ultraviolet region.

Before the radiation from the mercury lamp which has passed through the cell reaches the diffraction
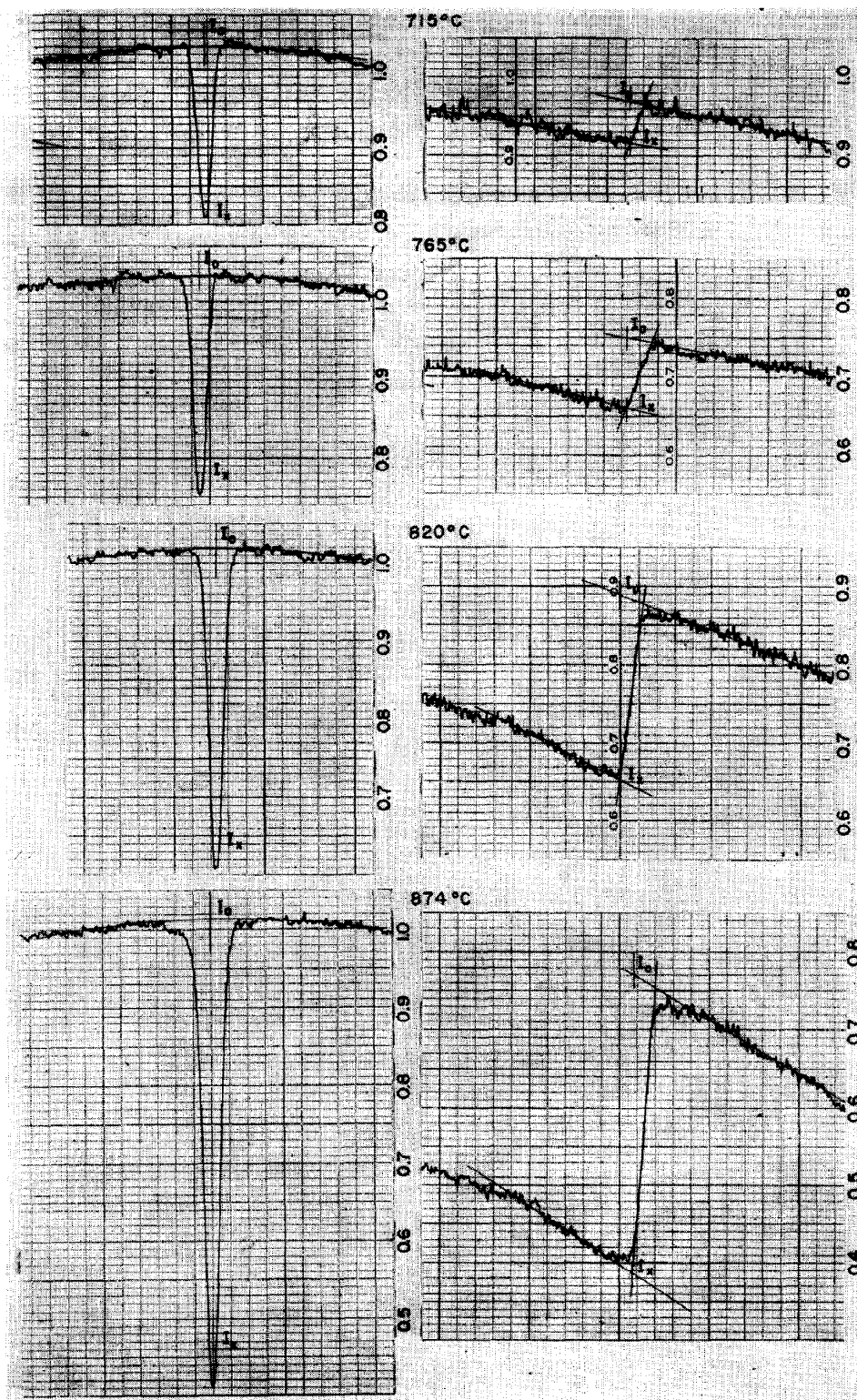
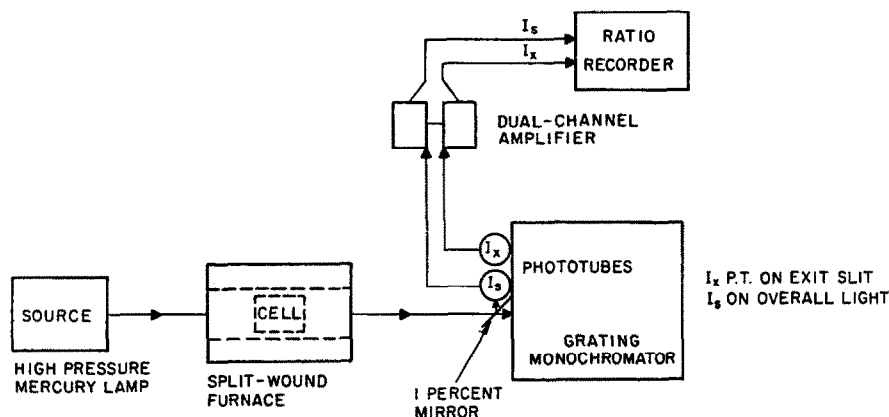Fig. 1. Representative absorption transitions of bismuth vapor at 3067 and 2731 Å.

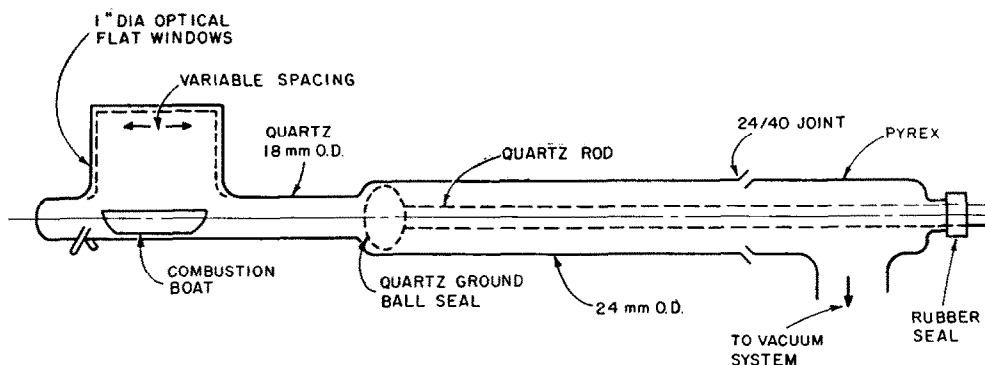FIG. 2. Schematic diagram of apparatus.



FIG. 3. Quartz cell.

grating, approximately 1 per cent is reflected by a mirror in front of the entrance slit to a reference phototube called $I_s$. The remaining radiation passes through the spectrograph and is recorded by the phototube marked $I_x$ which is placed at the exit slit. The radiation striking the $I_s$ tube will be multi-wavelength from approximately 2500–4000 Å. The light striking the $I_x$ phototube will correspond to radiation in an extremely small wavelength region.

The signals from the two phototubes are put into a dual-channel amplifier. The power input to the phototubes can be adjusted so that at any particular reading the intensity of the two signals in the amplifier can be balanced. The output from the dual-channel amplifier is recorded on a ratio recorder. The ratio recorder will read the intensity of phototube $I_x$ or the intensity of phototube $I_s$. It will also read the ratio of $I_x/I_s$ directly. Hence the recording system will give a trace of the intensity ratio $I_x/I_s$ as a function of wavelength. By splitting up the radiation before it enters the monochrometer, a reproducible intensity is assured for measurements from day to day. The instrument is set to scan in a particular wavelength region at a speed of 2.9 Å/min.

## CALIBRATION

An optical absorption measurement was made of pure mercury to check the apparatus. The slope of the line from a plot of log $(\beta p)$ versus $1/T$ for this experiment is a measure of the enthalpy of evaporation of mercury. From the Clausius–Clapeyron equation:

$$\log\left(\frac{\beta p_2}{\beta p_1}\right) = \frac{\Delta H_v}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

where $\beta p_i = (T \log I_0/I_x)_i$.

The value obtained was 72.0 cal/g. The accepted value is 72.6 cal/g in this temperature range.

In the measurement of the activity of bismuth in the liquid, either species can be used, although the $Bi_2$ provides a more sensitive measure since it is a measure of the square of the bismuth activity in the liquid. This is demonstrated by the following equations:

$$Bi(l) = Bi(v)$$

$$K_1 = \frac{a_{Bi(v)}}{a_{Bi(l)}} = \frac{p_{Bi(v)}}{a_{Bi(l)}}$$

$$2\,Bi(l) = Bi_2(v)$$

$$K_2 = \frac{a_{Bi_2(v)}}{[a_{Bi(l)}]^2} = \frac{p_{Bi_2(v)}}{[a_{Bi(l)}]^2}.$$

Measurements were made on the Pb–Bi system to check out the experimental apparatus and theory. Activities were calculated from relative measurements of the $Bi_2$ species for two alloys in the temperature range of 1018–1143 °K. The activities in this system have also been measured using the e.m.f. method. There was very good agreement between the two methods.

## ANALYSIS OF EXPERIMENTAL PROCEDURE

With the apparatus in proper alignment, measurements were made on various uranium–bismuth compositions as a function of temperature. The pure elements uranium and bismuth as well as uranium-bismuth alloys were placed in a boat and inserted in the cell as shown in Fig. 3. The cell was evacuated with a plunger out of the sealing position. After a vacuum of less than 1 $\mu$ was obtained in the cell, the plunger was inserted in the sealing position and the alloy heated to the desired temperature. At the temperature of measurement the cell system was maintained under static vacuum. Hence equilibrium conditions were obtained within the cell. Measurements of the atomic and diatomic absorption of bismuth vapor were made both on the heating cycle and cooling cycle. There was no difference observed in the readings. It was found in the temperature range of 700–1000°C that vapor–liquid equilibrium was established in less than 1 hr. Repeat readings over a period of 12 hr showed no change. In this study readings were taken at 15–30°C intervals with 1½ hr allowed for equilibrium between measurements.

### Preparation of alloys

The metals used in this study were 99.998 per cent pure bismuth guaranteed by the Belmont Smelting Company and 99.97 per cent pure uranium supplied by Mallinckrodt Chemical Company. All bismuth used in the study was vacuum melted and recast. The uranium was cleaned by an electrolytic technique to remove all surface oxide.

Uranium–bismuth alloys in the liquid and liquid + $UBi_2$ region were made-up in 25-g ingots by high-vacuum induction heating. Very clean alloys were obtained in the composition range 0–30 per cent uranium by vacuum-melting selected compositions of bismuth and uranium. The alloy ingots were easy to cleave because of the $UBi_2$ plate formation. Hence a 3–5 g sample of the uranium–bismuth alloy could be taken from an ingot, weighed, put in a recrystallized alumina boat and inserted in the quartz absorption cell for measurement. For compositions greater than

30 per cent uranium this technique was not found feasible. Because of the severe pyrophoric nature of uranium–bismuth alloys it was not possible to make an air transfer of a uranium–bismuth ingot of greater than 30 per cent uranium. Upon exposure to air the alloy immediately oxidized and disintegrated. In order to combat the air transfer problem and to avoid the complicated equipment for vacuum or inert-gas transfer of the sample, the alloys were made in the cell directly. To reach liquid conditions for high uranium alloys, a temperature of 1450°C is necessary as can be seen from the uranium–bismuth phase diagram (Fig. 4). Since this is an intolerable temperature for the quartz absorption cell, it was necessary to make the alloys by diffusion of bismuth into solid uranium. To facilitate the formation of the alloys a temperature of 925°C was used. The uranium used was cut into spirals of less than 1 mm thickness. Uranium–bismuth alloys can be made easily under these conditions.

It should be noted that the optical absorption method provides an excellent indication of the attainment of equilibrium. Upon reaching the alloying temperature, a line intensity reading is taken. This measurement is repeated until the readings become uniform. In the case of making uranium–bismuth alloys it is possible to watch the phase–composition changes going across the phase diagram. For example, in making a composition in the UBi + U region it was
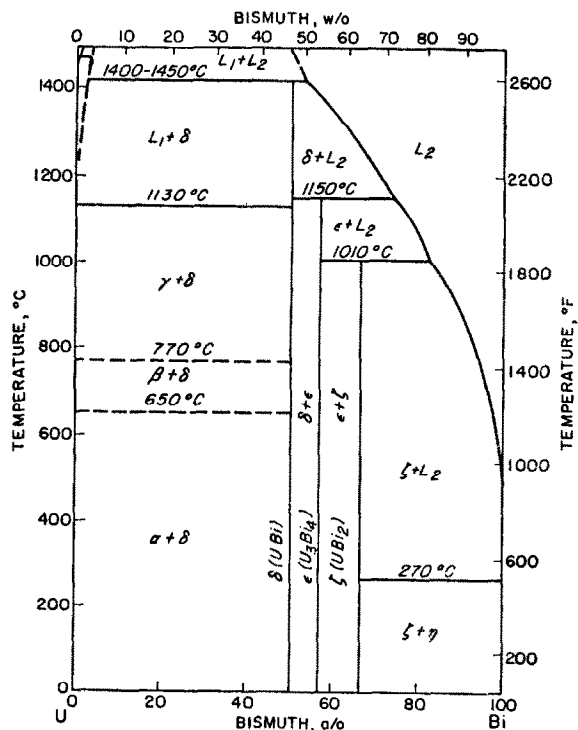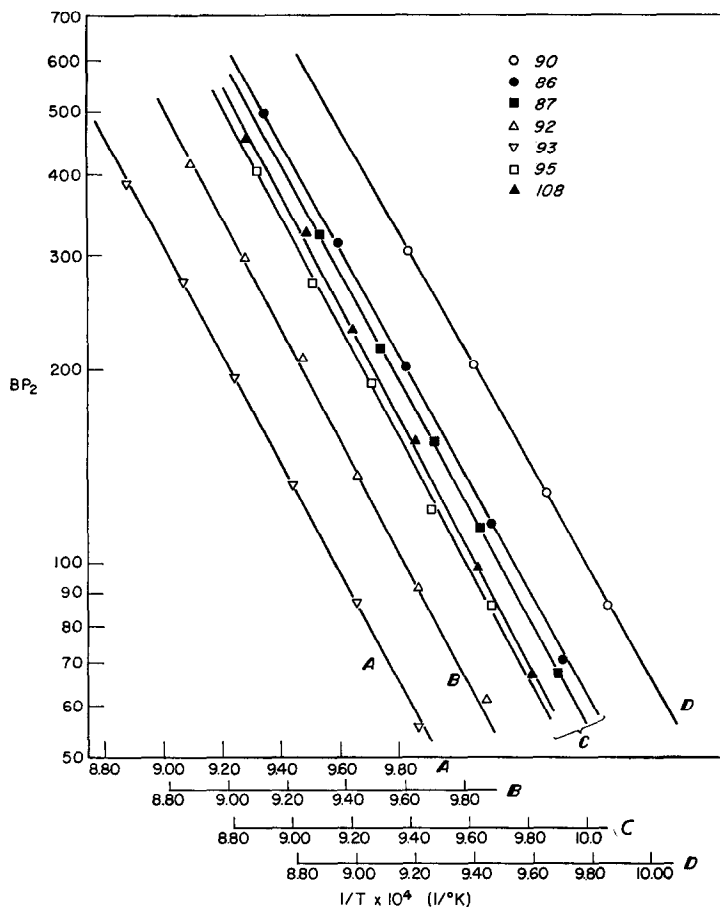


FIG. 4. Phase diagram.

FIG. 5. Representative data obtained for measured bismuth pressures in equilibrium with uranium–bismuth alloys.

possible to see the vapor pressure diminution of bismuth as the composition of the uranium–bismuth solid changed from one phase-region to the next.

*Activity measurements*

As discussed earlier, the thermodynamic activity can be calculated from measurement of either species of bismuth vapor. The $Bi_2$ measurement provides a more sensitive measure since a ratio of the bismuth vapor pressure above an alloy to that of pure bismuth is a measure of the square of the activity ratio in the two states.

Activities were determined by measurement of only the $Bi_2$ species in the composition ranges: liquid, liquid + $UBi_2$, and $UBi_2$ + $U_3Bi_4$. In the two remaining solid composition ranges not enough $Bi_2$ vapor was present to get an accurate measurement of thermodynamic activity. Hence, it was necessary to measure the thermodynamic activity by observing changes in the Bi vapor species.

Since the absorption of the light is a function of the number density and the cell length, the method for Bi measurement was calibrated by measuring the difference in optical absorption by changing cell length. This was done in order to eliminate error in the Bi measurement should the Beer–Lambert absorption law not hold rigorously for the atomic species.

The compositions $U_3Bi_4$ + UBi and UBi + U were run in two cells of different cell window spacing. The same alloy composition was run in cells of 46-mm and 15-mm cell window spacing. By subtracting the results obtained with a 15-mm cell from those obtained with a 46-mm cell and comparing the difference to pure bismuth, the thermodynamic activity could be calculated.

## RESULTS

The thermodynamic activity of bismuth was measured at temperatures from 725 to 875°C in the regions of $U_3Bi_4$ + $UBi_2$, $UBi_2$ + liquid and the one-phase, liquid region. Representative data for some alloys in these regions are shown in Fig. 5. The relationship of $\beta\, p_2$ with $1/T$ remained linear throughout the temperature range.

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TABLE 1. Summarized bismuth activity data

| Composition region | Run No. | Uranium (wt.%) | Mole fraction uranium $x_U$ | Bismuth activity | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | 1115°K | 1089°K | 1064°K | 1041°K | 1018°K |
| Liquid | 86 | 1.26 | 0.0111 | 0.990 | 0.990 | 0.984 | 0.980 | 0.977 |
| | 50 | 2.42 | 0.0213 | 0.975 | 0.971 | 0.970 | 0.969 | 0.967 |
| | 87 | 4.02 | 0.0355 | 0.954 | 0.950 | 0.941 | 0.932 | 0.930 |
| | 76 | 6.39 | 0.0565 | 0.940 | 0.925 | 0.911 | 0.909 | 0.903 |
| | 108 | 7.28 | 0.0644 | 0.905 | 0.892 | 0.878 | 0.863 | 0.851 |
| | 70 | 8.13 | 0.0721 | 0.897 | 0.868 | 0.863 | 0.853 | 0.846 |
| $UBi_2$ + Liq. | 92 | 14.6 | 0.131 | 0.877 | 0.868 | 0.858 | 0.842 | 0.834 |
| | 71 | 16.3 | 0.146 | 0.864 | 0.855 | 0.850 | 0.838 | 0.832 |
| | 93 | 17.1 | 0.153 | 0.853 | 0.850 | 0.840 | 0.832 | 0.824 |
| | 95 | 29.5 | 0.269 | 0.865 | 0.858 | 0.846 | 0.836 | 0.828 |
| | Avg. | | | 0.865 | 0.858 | 0.849 | 0.837 | 0.829 |
| $UBi_2$ + $U_3Bi_4$ | 96 | 44.5 | 0.413 | 0.534 | 0.498 | 0.461 | 0.429 | 0.401 |
| | 97 | 42.6 | 0.394 | 0.539 | 0.513 | 0.485 | 0.459 | 0.435 |
| | Avg. | | | 0.537 | 0.506 | 0.473 | 0.444 | 0.418 |
| $U_3Bi_4$ + UBi | 103 104 106 | 50.4 50.6 50.0 | | 0.0813 | 0.0630 | 0.0493 | 0.0393 | 0.0306 |
| U + UBi | 99 100 | 68.2 67.9 | | 0.0246 | 0.0189 | 0.0147 | 0.0116 | 0.0088 |

In order to obtain measurable quantities in the regions UBi + U and UBi + $U_3Bi_4$ it was necessary to work at temperatures from 800 to 1000°C. The results of all the measurements are summarized in Table 1. The thermodynamic activity of bismuth is given as a function of composition at five different temperatures: 1018, 1041, 1064, 1089 and 1115°K.

The activity of bismuth in the liquid region shows a significant negative deviation from Raoult's law. The deviation becomes more negative at lower temperatures. From a graphical correlation of the activity of bismuth in the liquid phase as a function of composition, the solubility of uranium in bismuth at a particular temperature can be estimated:

| $x_U$ | Temp. (°K) |
|---|---|
| 0.087 | 1115 |
| 0.076 | 1089 |
| 0.073 | 1064 |
| 0.069 | 1041 |
| 0.066 | 1018 |

From a knowledge of the thermodynamic activity of bismuth in the uranium–bismuth system, the activity of uranium for the entire system can be determined by an integration of the Gibbs–Duhem equation. In the liquid composition range the uranium activities were determined by integrating the Gibbs–Duhem equation with a modified alpha-function.[3] A constant value of alpha was calculated for each of the

five temperatures reported. The integration was performed from the solubility limit of uranium in bismuth to the composition of pure bismuth. The integration was carried out in detail for five different temperatures. The liquid uranium–bismuth compositions were found not to obey regular solution behavior.

The uranium activities in the two-phase region (constant activity) were determined by a graphical integration of the partial molar free energies of bismuth in the respective two-phase regions. Fig. 6 shows the construction lines for determining the partial molar free energy of uranium. The mathematical equations for this construction are given in Ref.(4).

The activities calculated for uranium are summarized in Table 2 and the partial molar free energies are listed in Table 3.

From a knowledge of the partial molar free energy of uranium and bismuth, the partial molar entropy of each constituent can be calculated. The partial molar entropy of any constituent is given by the following equation:

$$\Delta \bar{S}_i = - \frac{\delta \Delta \bar{F}_i}{\delta T}.$$

In the temperature range employed, the partial molar entropy of bismuth and uranium was found to be constant. From the calculation of the partial molar entropy of bismuth, the partial molar entropy of uranium can be determined by a graphical construction as performed for the partial molar free energy
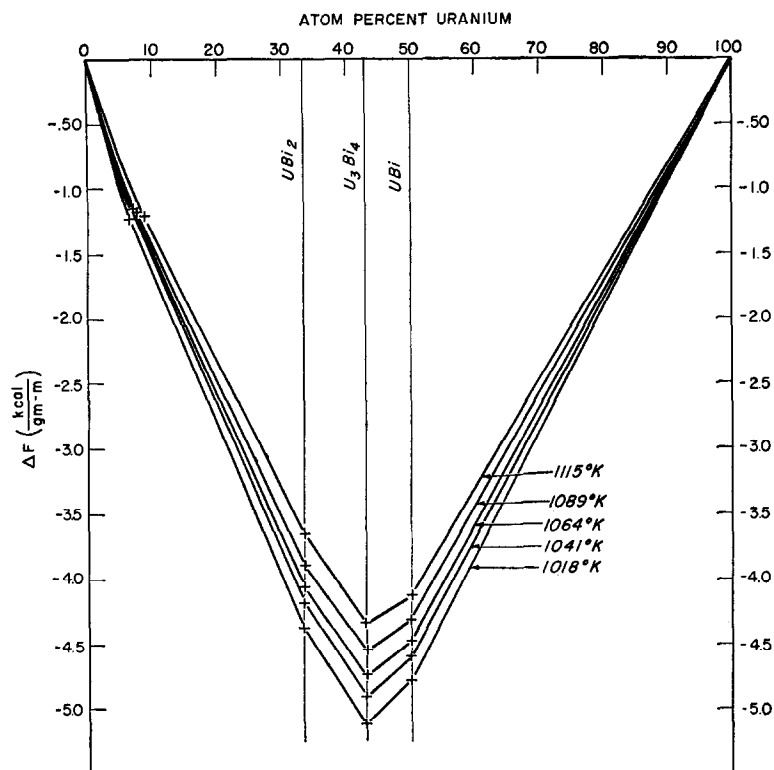
**ATOM PERCENT URANIUM**



FIG. 6. Integral molar free energy diagram for the U–Bi system.

TABLE 2. Activity of uranium

| Temperature (°K) | Composition | | | |
|---|---|---|---|---|
| | UBi + U | $U_3Bi_4$ + UBi | $UBi_2$ + $U_3Bi_4$ | $UBi_2$ + Liq. |
| 1115 | 1.0 | $3.02 \times 10^{-1}$ | $2.46 \times 10^{-2}$ | $9.33 \times 10^{-3}$ |
| 1089 | 1.0 | $3.00 \times 10^{-1}$ | $1.86 \times 10^{-2}$ | $6.31 \times 10^{-3}$ |
| 1064 | 1.0 | $2.97 \times 10^{-1}$ | $1.45 \times 10^{-2}$ | $4.27 \times 10^{-3}$ |
| 1041 | 1.0 | $2.95 \times 10^{-1}$ | $1.17 \times 10^{-2}$ | $3.39 \times 10^{-3}$ |
| 1018 | 1.0 | $2.87 \times 10^{-1}$ | $8.71 \times 10^{-3}$ | $2.19 \times 10^{-3}$ |

TABLE 3. Partial molar free energies (kcal/g-mole)

Bi(l) = Bi(in alloy) (s)

U(s) = U(in alloy) (s)

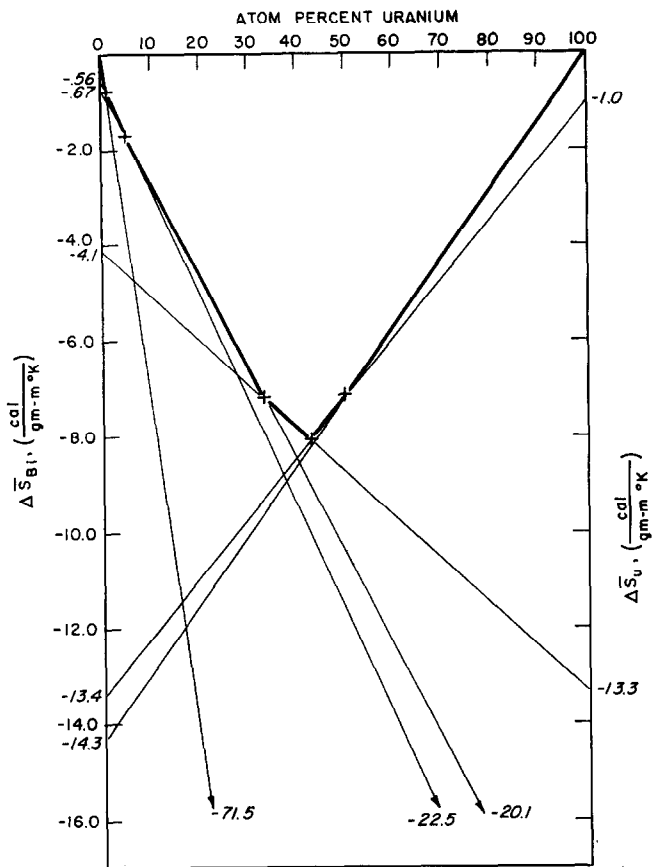| Composition | | 1018°K | 1041°K | 1064°K | 1089°K | 1115°K |
|---|---|---|---|---|---|---|
| UBi + U: | | | | | | |
| | Bi | −9.58 | −9.21 | −8.91 | −8.61 | −8.22 |
| | U | 0 | 0 | 0 | 0 | 0 |
| $U_3Bi_4$ + UBi: | | | | | | |
| | Bi | −7.06 | −6.69 | −6.36 | −6.0 | −5.56 |
| | U | −2.53 | −2.52 | −2.56 | −2.61 | −2.66 |
| $UBi_2$ + $U_3Bi_4$: | | | | | | |
| | Bi | −1.77 | −1.68 | −1.58 | −1.48 | −1.38 |
| | U | −9.61 | −9.20 | −8.95 | −8.65 | −8.22 |
| $UBi_2$ + Liq: | | | | | | |
| | Bi | −0.38 | −0.37 | −0.346 | −0.334 | −0.32 |
| | U | −12.4 | −11.75 | −11.53 | −10.98 | −10.4 |
| $x_U = 0.05$: | | | | | | |
| | Bi | −0.224 | −0.219 | −0.185 | −0.174 | −0.158 |
| | U | −15.1 | −14.7 | −14.5 | −13.5 | −13.2 |
| $x_U = 0.01$: | | | | | | |
| | Bi | −0.0326 | −0.033 | −0.0292 | −0.025 | −0.026 |
| | U | −22.9 | −22.2 | −21.15 | −19.0 | −18.2 |

Fig. 7. Integral molar entropy diagram for the U–Bi system.

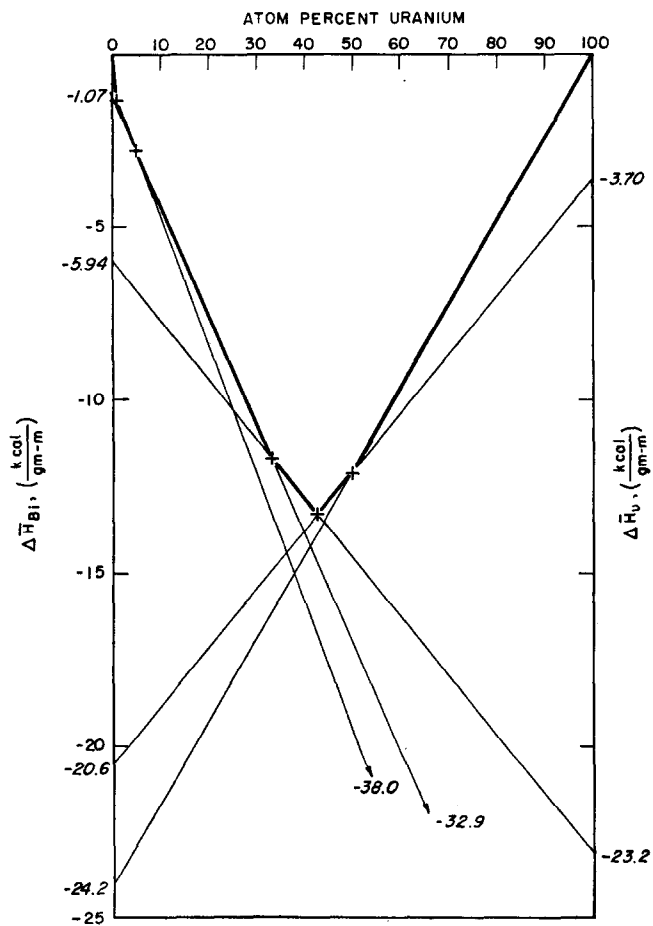Fig. 8. Integral molar enthalpy diagram for the U–Bi system.

TABLE 4. Integral molar quantities
$(1 - x)\text{Bi(l)} + x\text{U(s)} \rightarrow \text{U}_x\text{Bi}_{1-x}\text{(s)}$

| Mole fraction $x_U$ | $\Delta F$ (kcal/g-mole) | | | | | $\Delta S$ (cal/g-mole °K) | $\Delta H$ (kcal/g-mole) |
|---|---|---|---|---|---|---|---|
| | 1115°K | 1089°K | 1064°K | 1041°K | 1018°K | 1018 → 1115°K | 1018 → 1115°K |
| 0.10 | −1.33 | −1.39 | −1.46 | −1.50 | −1.61 | −2.65 | −4.31 |
| 0.20 | −2.35 | −2.49 | −2.58 | −2.64 | −2.80 | −4.60 | −7.50 |
| 0.30 | −3.32 | −3.52 | −3.68 | −3.79 | −3.98 | −6.50 | −10.70 |
| 0.40 | −4.12 | −4.34 | −4.53 | −4.67 | −4.89 | −7.80 | −12.85 |
| 0.50 | −4.12 | −4.31 | −4.48 | −4.60 | −4.78 | −7.15 | −12.10 |
| 0.60 | −3.30 | −3.44 | −3.58 | −3.69 | −3.82 | −5.75 | −9.59 |
| 0.70 | −2.45 | −2.60 | −2.68 | −2.76 | −2.84 | −4.30 | −7.23 |
| 0.80 | −1.64 | −1.72 | −1.78 | −1.83 | −1.89 | −2.85 | −4.79 |
| 0.90 | −0.82 | −0.87 | −0.90 | −0.91 | −0.96 | −1.40 | −2.57 |

(Fig. 7). The standard states are taken as bismuth (liquid) at that temperature and uranium (solid) at that temperature in its particular crystal modification.

From the definition $\Delta \bar{H}_i = \Delta \bar{F}_i + T\Delta \bar{S}_i$, the partial molar enthalpy of both constituents can be calculated from a summation of $\Delta \bar{F}_i$ and $T\Delta \bar{S}_i$. The results are shown graphically in Fig. 8.

From the construction diagrams for the partial molar quantities, the integral molar quantities for the solutions can be determined. The results are given in Table 4.

As indicated previously for the partial molar entropy quantities, the integral molar entropy is constant over the measured temperature range. The integral molar
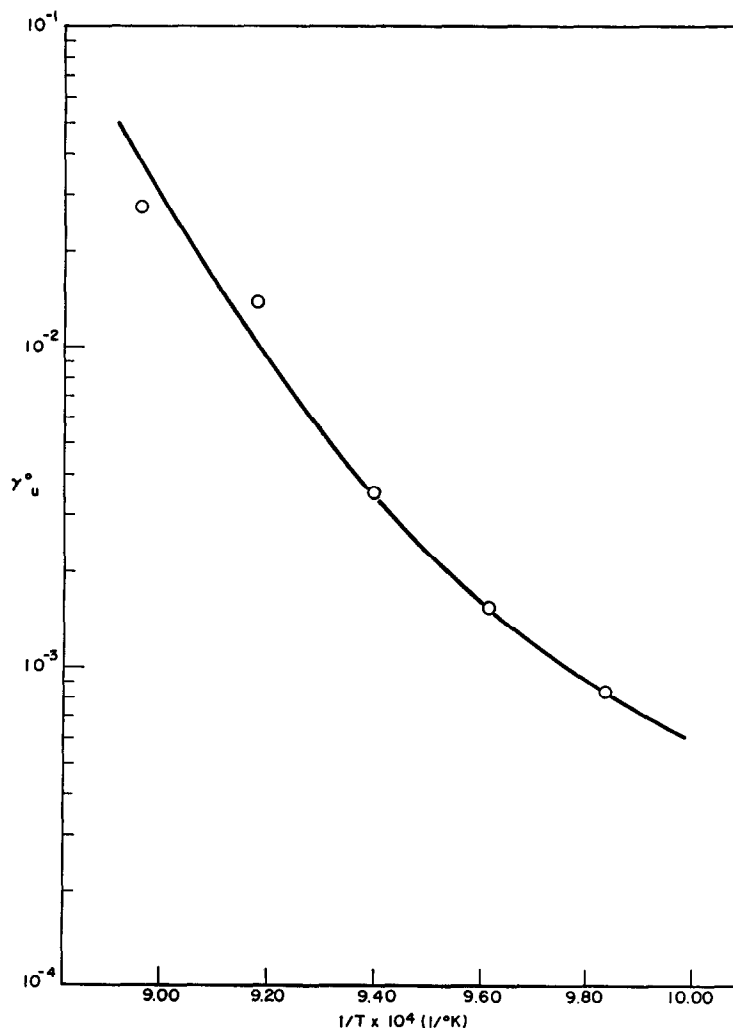


FIG. 9. Henry's Law parameter versus $(1/T \times 10^4)$ $1/°K$.

enthalpy was also found to be constant in the temperature range employed.

An attempt was made to correlate the regular solution parameter for dilute solutions of uranium in bismuth as a function of temperature. A correlation is shown graphically in Fig. 9. Since the correlation is not linear, it may be concluded that the Hildebrand regular solution criterion does not hold for dilute solutions of uranium in bismuth. The Henry's law parameters, $\gamma_U{}^0$, are valid in the very dilute regions only. The parameter is not valid for uranium concentrations greater than 2 mole%.

## DISCUSSION

A summary is made in Table 5 of the thermodynamic activity obtained in this study and that obtained by Gross et al.[5] at 742°C. A significant difference is to be noted between the two results. This is particularly true in the composition range U + UBi. Gross et al. obtained their data by an effusion technique and use of equilibrium data obtained by Yoshiyama[6].

TABLE 5. Bismuth activity in uranium–bismuth alloys at 742°C

| Composition | This study | Ref. (5) |
|---|---|---|
| U + UBi | $8.8 \times 10^{-3}$ | $8.7 \times 10^{-4}$ |
| $UBi + U_3Bi_4$ | 0.0306 | 0.12 |
| $U_3Bi_4 + UBi_2$ | 0.418 | 0.29 ($U_3Bi_4 + U_3Bi_5$) |
|  |  | 0.69 ($U_3Bi_5 + UBi_2$) |
| $UBi_2 + Liq$ | 0.829 | $0.95_5$ |

The composition $U_3Bi_5$ reported by Gross et al. was not found in this investigation. The compound $U_3Bi_5$ has been considered by various investigators. However, the investigators of the phase diagram of the uranium–bismuth system, Teitel[7] and Coterill[8] have not reported the existence of a $U_3Bi_5$ compound.

As was pointed out earlier, in making up alloys in the uranium-rich region of the diagram, weighed compositions of uranium spirals and bismuth metal were placed in the cell, heated to 925°C and allowed to equilibrate. In the course of diffusion, the transformations across the phase diagram to the desired alloy were observed in definite steps in the bismuth vapor pressure. In no case was there a measured pressure found corresponding to or indicating the presence of a $U_3Bi_5$ compound.

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## NOMENCLATURE

| | |
|---|---|
| $a_i$ | thermodynamic activity of component $i$ |
| $Ap_1$ | measured pressure of Bi |
| $\beta p_2$ | measured pressure of $Bi_2$ |
| $\Delta F$ | free energy of formation |
| $\Delta \bar{F}_i$ | relative partial molar free energy |
| $\Delta H$ | enthalpy of formation |
| $\Delta \bar{H}_i$ | relative partial molar enthalpy |
| $I_0$ | intensity of incoming radiation |
| $I_x$ | intensity of radiation out of the cell |
| $\Delta S$ | entropy of formation |
| $\Delta \bar{S}_i$ | relative partial molar entropy |
| $x_i$ | mole fraction of component $i$ |
| $\gamma_i$ | activity coefficient of component $i$ |
| $T$ | temperature (°K) |