

FIG. 2. Contact zones (shaded) of spherical particles O_1 and O_2 of radius R .

0.05μ by means of electron microscope photographs. The surface area, $10.6 \text{ m}^2/\text{g}$, determined from the BET plot in the range of relative pressure $x < 0.05$ is essentially in agreement with that obtained from the particle size, $15.6 \text{ m}^2/\text{g}$. We adopted $R = 0.07\mu$ as the radius of the particles in order to match the more reliable BET area. The steep slope of the curve near $x=1$ may be attributed to capillary condensation in the contact zones of particles. In order to explore this idea, the volume $V(r)$ in the contact zones has been calculated geometrically as a function of radius (r) of meniscus formed, as shown in Fig. 2. The particles are assumed, as a first approximation, to be spherical and of equal radius R . The $V(r)-r$ relation depends strongly on the type of packing. Therefore, we made calculations for three representative types: closest packing (C.P.), planar close packing (P.P.), and linear packing (L.P.). For C.P. and P.P., the volume $V(r)$ may conveniently be expressed in two terms, V_1 and V_2 . V_1 is the space within the contacting sphere O' , obtained by partially rolling O' around the line O_1-O_2 , and V_2 is essentially the space enclosed by the sphere O' and the powder particles. Formulas follow which give the volume $V(r)$ in cm^3 per unit true volume of powder particles, independent of their sizes, as a function of $y=r/R$.

(1) For linear packing.—

$$V(y) = V_1(y) = \frac{3}{2}y^2\{1 - [(\pi/2) - \theta][y(y+2)]^{\frac{1}{2}}\}; \quad \theta = \arccos(1+y)^{-1}.$$

(2) For planar close packing.—

(a) If $y \leq y_1 = 0.15470$, $V(y) = 3V_1(y)$. Note that r_1 is the radius of the small circle shown in Fig. 2, contacting the cross section of three particles.

(b) If $y > y_1$, $V(y) = V_1(y) + V_2(y)$;

$$V_1 = (9/\pi)\Theta y^2\{1 - [(\pi/2) - \theta][y(y+2)]^{\frac{1}{2}}\};$$

$$V_2 = (9/2\pi)\left\{\frac{1}{3}[3y(y+2) - 1]^{\frac{1}{2}} + 2\Theta + (\pi/3)y^3 - (y^3+1) \arccos\left(\frac{1-(y+1)^2}{2y(y+2)}\right)\right\};$$

$$\Theta = (\pi/2) - \arcsin(1 - \frac{1}{3} \tan^{-2}\theta)^{\frac{1}{2}}.$$

(3) For closest packing.—

(a) If $y \leq y_1$, $V(y) = 6V_1(y)$.

(b) If $y_1 < y \leq y_2 = 0.22475$, $V(y) = 2V_1 + 4V_2$.

(c) If $y_2 < y \leq y_3 = 0.4142$

$$V(y) = \frac{1}{2}V_1 + 4V_2 - (9/\pi)\{1 - [(\pi/2) - \theta][y(y+2)]^{\frac{1}{2}}\}\Theta_2 + [2y^3 + 4V_2(y=y_2)];$$

$$\Theta_2 = \Theta(y=y_2) = 0.61555;$$

$$[2y_2^3 + 4V_2(y=y_2)] = 0.0992 \text{ cm}^3/\text{cm}^3.$$

Note that $r_2(=y_2R)$ and $r_3(=y_3R)$ are the radii of spherical holes, which inevitably exist in closest packing, contacting, respectively, 4 and 6 particles.

The formula for the vapor pressure depression of the condensed sorbate in the contact zones may be subject to some uncertainty. If we adopt the Thomson equation, $x = \exp(-2\gamma v/rkT)$, for the

sake of simplicity as well as appropriate *à posteriori* reasons, we can easily obtain the theoretical isotherm due to capillary condensation for any given sorption system, on the basis of the $V(y)-y$ relation mentioned above. In Fig. 1 are represented such theoretical isotherms for the present system. The capillary condensation is added on to a monolayer of the sorbate, which is complete at low pressure. Experimental points, denoted by \circ or \ominus , lie essentially on the theoretical curve for planar close packing. The agreement supports the idea of capillary condensation in the contact zones of particles even though they are non-porous. Similar results were reported by Holmes and Emmett¹ in the adsorption of nitrogen on two samples of glass spheres whose radii are 3.5 and $1.5-2.5\mu$. They also concluded that the adsorption near saturation was due to capillary condensation. Our calculation confirms their conclusion, exhibiting good agreement in the region higher than $x \approx 0.99$, as shown in Fig. 3.

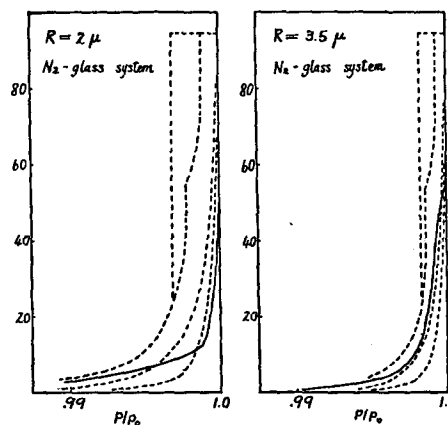


FIG. 3. Adsorption isotherms for N_2 on glass spheres. Solid lines, experimental data (see reference 1); dotted lines, theoretical isotherms for closest packing, planar close packing, and linear packing, respectively.

In view of these satisfactory results, we might conclude that if particle sizes are reduced sufficiently, nonporous particles can give rise to a marked capillary condensation in their contact zones. If this is valid, we may say that the multilayer adsorption does not occur at least for the anatose-ethyl alcohol system. Details will be published elsewhere.

In conclusion, the authors wish to express their sincere thanks to Professor F. Ishikawa for his helpful advice and encouragement. We are also indebted to Professor P. H. Emmett for helpful criticism of this note.

¹ J. Holmes and P. H. Emmett, *J. Phys. Colloid Chem.* **51**, 1262 (1947).

The Crystallography of Nickel Kieselguhr*

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AN x-ray investigation was made of a nickel kieselguhr substance used as a catalyst in organic hydrogenation reactions. Nickel kieselguhr is a diatomaceous earth upon, and in which, nickel has been chemically deposited. The investigation shows Ni and NiO are present and that there is no significant change in lattice parameter in either of these substances. NiO is present in sufficient amounts to give powder lines of appreciable intensity.

This analysis is different from that of de Lange and Visser's (1946) work on nickel catalysts deposited on kieselguhr.¹ They state that the normal lattice of metallic Ni does not occur in materials prepared in this way, and the reduced active catalyst is a result of the attack of hydrogen on a nickel hydrosilicate.

Certain crystal planes are common to both the face-centered cubic Ni and to the ideal hexagonal close-packed Ni, so that their interplanar spacings check exactly (for example, face-centered cubic 111 and the hexagonal close-packed 0002). The additional cubic Ni powder lines and the powder lines of NiO have interplanar spacings which approximate those of the hexagonal close-packed structure.² Accordingly, on a poor quality powder film of a mixture of Ni and NiO, especially one taken with a short x-ray wavelength which would cause a crowding together of the lines, the composite pattern might have been mistakenly indexed as belonging to a hexagonal close-packed structure. It thus appears to the writer that the much debated form of hexagonal close-packed nickel might be the result of a wrong interpretation of what are actually lines belonging to Ni and NiO.

The size of the Ni and NiO particles are of colloidal dimensions and result in definite line broadening on the film. The particle sizes were determined by methods outlined in James.³ Owing to the interchangeability of indices in the cubic system it is impossible to give definite values for the length of a particular axis or the thickness of the particle in a given direction. However, it is possible to determine an average volume and thus the linear dimension of the particles. The linear dimension of the particles was found to be of the order of magnitude of 330Å and 160Å for the Ni and NiO particles, respectively. The linear dimension is by definition the cube root of the volume.

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¹ J. J. de Lange and G. H. Visser, *Ingenieur (Utrecht)* **58**, No. 26, 24 (1946).

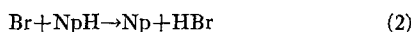
² H. S. Rawdon and H. C. Vacher, *Metal Progress*, 40 (1941).

³ R. W. James, *The Optical Principles of the Diffraction of X-Rays* (G. Bell and Sons, Ltd., London, 1948).

On the Bromination of Neopentane

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IN recent work on the bromination of neopentane,^{1,2} the rate-determining step in the chain



is assigned a frequency factor of 9.34×10^{16} cc mole⁻¹ sec⁻¹ and an activation energy of 18.1 kcal at 197.4°C. Both values are inconsistent with values obtained from the bromination of H₂, CH₄, and C₂H₆ shown in Table I.

The steric factor derived from the above frequency factor is 473, an impossible value for a single, bimolecular step reaction. All other work on such radical reactions have shown steric factors considerably less than unity.³ Since neopentane bromination is faster than that of H₂ or CH₄ and the chain breaking efficiency is greater for the former, the chain must be faster and thus the activation energy of reaction 2 must be smaller than 18.1 kcal.

TABLE I. Br + XH → HBr + X.

X	Range studied °C		ΔH _f ⁰ kcal/mole	E _a kcal/mole	A cc mole ⁻¹ sec ⁻¹
	Photo-chemical	Thermal			
H ₂ , b, e	433-499	470-575	16.7	17.5	1.14 × 10 ¹²
CH ₄ ^c	423-503	570	12.3	17.8	1.48 × 10 ¹²
C ₂ H ₆ ^d	308-363	...	8.3	13+	...
Np ^f	371-470	470	-1.6 + H _f ⁰ (Np)	18.1	9.34 × 10 ¹⁶

^a M. Bodenstein and S. C. Lind, *Z. physik. Chem.* **57**, 168 (1906).

^b M. Bodenstein and H. Lutkemeyer, *Z. physik. Chem.* **114**, 208 (1924).

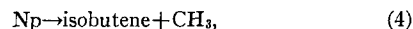
^c G. B. Kistiakowsky and E. R. Van Artsdalen, *J. Chem. Phys.* **12**, 469 (1944).

^d H. C. Anderson and E. R. Van Artsdalen, *J. Chem. Phys.* **12**, 469 (1944).

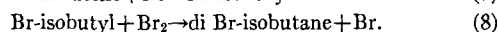
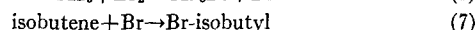
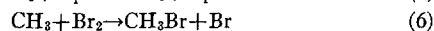
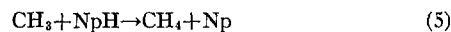
^e See reference 1.

^f See reference 2. ΔH_f⁰ based on N.B.S. tables except for H_f⁰ of CH₄ and C₂H₆ which were taken from Swarc, *Chem. Revs.* **47**, 75 (1950).

A possible explanation of the above anomaly lies in the rather interesting reaction of the neopentyl radical



followed by



Reaction 4 is expected to have an activation energy of about 23 kcal⁴ and assuming the usual unimolecular frequency factor of 10¹³ sec⁻¹ will compete with other reactions of the Np radical.

When reactions 4 to 8 are included in the scheme postulated by the original workers^{1,2} a new rate expression is obtained from which an activation energy for reaction 2 can be estimated of about 12 ± 2 kcal. This still leads to a steric factor of near unity which although probably too high is at least within the limits of experimental error and uncertainty in the chain mechanism.⁵

¹ E. I. Hormats and E. R. Van Artsdalen, *J. Chem. Phys.* **19**, 778 (1951).

² F. E. Schweitzer and E. R. Van Artsdalen, *J. Chem. Phys.* **19**, 1028 (1951).

³ E. W. R. Steacie and M. Swarc, *J. Chem. Phys.* **19**, 1309 (1951).

⁴ S. Bywater and E. W. R. Steacie, *J. Chem. Phys.* **19**, 319 (1951). They give a value of 23 kcal for the scission of C₂H₇ into CH₃ + C₂H₄.

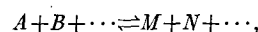
⁵ It is to be noted that no analyses were made of the products of the reaction by the original authors.

Chemical Reactions near Equilibrium

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IN seeming contradiction to usual deductions from thermodynamics, it has been shown by De Donder¹ on the basis of his affinity function, by Prigogine² on the basis of the Chapman-Enskog model, and by Manes, Hofer, and Weller³ using purely mathematical methods, that the rate of a chemical reaction close to equilibrium is directly proportional to the free energy difference between reactants and products. This relation may be shown to be a consequence of the theory of absolute reaction rates, also.

If one has the generalized reaction



$$\Delta F_f^\ddagger = \Delta F_f^{\ddagger 0} + RT \ln Q_f^\ddagger = \Delta F_f^{\ddagger 0} + RT \ln \frac{a^\ddagger}{a_A a_B \dots}$$

$$\Delta F_r^\ddagger = \Delta F_r^{\ddagger 0} + RT \ln Q_r^\ddagger = \Delta F_r^{\ddagger 0} + RT \ln \frac{a^\ddagger}{a_M a_N \dots},$$

where ΔF_f^\ddagger is the free energy of activation of the forward reaction at any concentration, ΔF_r^\ddagger is the free energy of activation of the reverse reaction at any concentration, $\Delta F_f^{\ddagger 0}$ is the standard free energy of activation of the forward reaction, and $\Delta F_r^{\ddagger 0}$ is the standard free energy of activation for the reverse reaction. a_i is the activity of the i th component and a^\ddagger is the activity of the activated complex.

We may now write the expressions for the rate constants of the forward and reverse reactions as

$$k_f = \kappa_f \frac{kT}{h} \exp\left(-\frac{\Delta F_f^{\ddagger 0}}{RT}\right); \quad k_r = \kappa_r \frac{kT}{h} \exp\left(-\frac{\Delta F_r^{\ddagger 0}}{RT}\right);$$

$$= \kappa_f \frac{kT}{h} Q_f^\ddagger \exp\left(-\frac{\Delta F_f^\ddagger}{RT}\right); \quad = \kappa_r \frac{kT}{h} Q_r^\ddagger \exp\left(-\frac{\Delta F_r^\ddagger}{RT}\right).$$

The expression for the rate of this reaction becomes

$$\frac{da_A}{dt} = \frac{da_B}{dt} = \dots = -\frac{da_M}{dt} = -\frac{da_N}{dt} = \dots$$

$$= k_f a_A a_B \dots - k_r a_M a_N \dots$$