JOURNAL OF CATALYSIS 39, 463–470 (1975)

The Physical Adsorption of 1,1,1-Trichloroethane on Uranium Dioxide[1]

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Received March 6, 1975

Adsorption isotherms for 1,1,1-trichloroethane adsorption on uranium dioxide were obtained gravimetrically in the temperature range 0–30°C. Adsorption data were evaluated using the BET and Clausius-Clapeyron equations and the potential theory of adsorption. The heat of adsorption was found to vary between 12 and 8 kcal/mole, depending upon the coverage. Using the BET equation the size of the adsorbed CH_3CCl_3 molecule was calculated to be 33 ± 5 Å^2.

INTRODUCTION

Chlorinated solvents are used extensively for vapor degreasing and other cleaning operations where a nonaqueous solvent is desired. Because of this broad spectrum usage it is desirable to understand the interaction of various solvents with solid surfaces. In the case of nuclear materials the effects of radiation as well as the oxide film present on the metal must be considered. For these materials one needs to know if the solvent will react with the oxide film or if it will adsorb strongly enough to permit significant radiolysis to take place.

Studies have already been made of the adsorption of carbon tetrachloride (*1*) and trichloroethylene (*2*) on uranium dioxide. However, from the standpoint of toxicity and stability the solvent which appears to be most suited for general use is 1,1,1-trichloroethane. The work described in this paper was undertaken to characterize the adsorption of 1,1,1-trichloroethane on uranium dioxide. Included in the investigation was the measurement of the adsorption isotherms for both argon and 1,1,1-trichloroethane and the calculation of the heat of adsorption and the size of the solvent molecule.

[1] Research performed under the auspices of the U.S. Energy Research and Development Administration Contract AT(29-1)-1106.

EXPERIMENTAL METHODS

Apparatus

The experimental system used for this study is shown in Fig. 1. Adsorption was measured gravimetrically using a Cahn Model RH recording microbalance. The weighing mechanism was enclosed in a glass chamber which was connected to a metal vacuum system. Both the sample and the counter weight were suspended in 55 mm internal diameter Pyrex tubes. Pressure within the system could be varied from 10^{-6} Torr to 1 atm. Measurement of the system pressure was made with an ion gauge in the 10^{-3}–10^{-6} Torr range and a Baratron Series 90 pressure meter for pressures greater than 10^{-3} Torr. Over the adsorption pressure range of 1–120 Torr the accuracy of the meter was ± 0.5 Torr.

During adsorption the temperature of the sample was controlled with a constant temperature bath to ± 0.1°C. The actual temperature of the sample was measured with a thermocouple located inside the hangdown tube and adjacent to the sample.

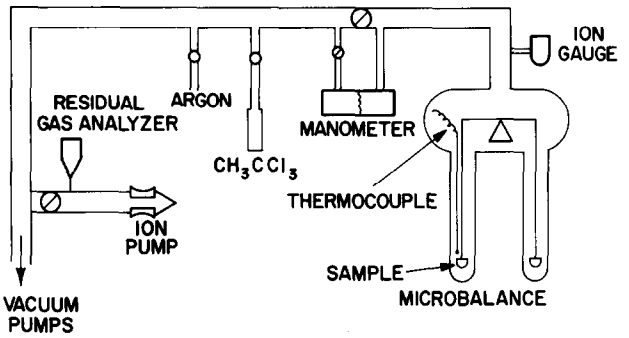

FIG. 1. Experimental system for the investigation of gas–solid interactions.

Materials

The UO_2 used for this study was the same as used for earlier studies (*1,2*). Analysis of this oxide showed the total impurity content to be 540 ppm. After loading the sample into the experimental system the oxide was conditioned by heating in air at 300°C for 2 hr followed by a 400°C vacuum bakeout for 15 hr. This 400°C outgassing step was also used after each adsorption run. Initially, there was some U_3O_8 present in the sample. However, X-ray diffraction analysis of the uranium oxide showed the composition to be UO_2 following the heat treatment.

Technical grade 1,1,1-trichloroethane (Chlorothene VG solvent from The Dow Chemical Co.) was used as the adsorbate. Inhibitors introduced into the solvent by the manufacturer included dioxane, nitromethane, and butylene oxide. The concentration of these inhibitors was not felt to be sufficient so as to interfere with the adsorption process. Prior to beginning the experiment the container of CH_3CCl_3 was outgassed to remove the air. This was accomplished by a series of freezing–evacuation–thawing cycles. Commercially available ultrapure argon was used for the surface area measurements.

Procedure

Before placing the sample on the balance a number of blank runs were made to determine the operational characteristics of the balance at different temperatures and pressures. The initial runs were made with empty buckets on the balance using either argon at −197.7°C or CH_3CCl_3 at 0, 15 and 30°C. The results obtained from these blank runs were invaluable to the experimental results ultimately obtained. Corrections for buoyancy and thermal effects obtained from the blank runs were then used to correct the actual adsorption data.

The first series of experiments were made using argon as the adsorbate with the sample in a liquid nitrogen bath. The actual sample temperature was determined by measuring the saturation vapor pressure of argon within the system. A reproducible vapor pressure of 149 Torr was measured which is equivalent to −197.7°C. Argon adsorption data were then used to calculate the surface area of the uranium dioxide.

The adsorption of 1,1,1-trichloroethane was measured at 0, 15 and 30°C. Vapor pressures for each run were varied between zero and the saturation vapor pressure. Desorption was accomplished by immersing the CH_3CCl_3 reservoir in liquid nitrogen. During the adsorption runs the weight change of the sample was monitored continuously.

RESULTS AND DISCUSSION

Argon Adsorption on Uranium Dioxide

Although the uranium dioxide sample had been previously used in adsorption

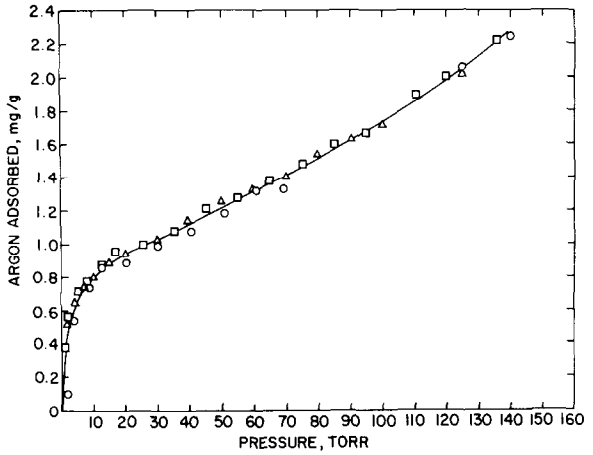

FIG. 2. Isotherm for the adsorption of argon on uranium dioxide at −197.7°C. Symbols denote multiple adsorption runs.

studies (*2*), the higher outgassing temperature used for this experiment necessitated a remeasurement of the oxide surface area. The argon adsorption isotherm is shown in Fig. 2. A comparison of this isotherm with the one obtained earlier (*2*) showed greater adsorption during the present experiment. However, this was most likely the result of the lower adsorption temperature, −197.7°C compared to −195.4°C. A BET plot of the adsorption data, Fig. 3, resulted in a current surface area of 1.75 m^2/g. For this calculation the size of the argon molecule was taken as 13.8 $Å^2$ (*3*). The difference between the measured uranium dioxide surface area for this and the previous experiment was 0.13 m^2/g. This was within the expected experimental error and indicated that increasing the outgassing temperature from 300 to 400°C had no effect on the surface area.

1,1,1-Trichloroethane Adsorption on Uranium Dioxide

Adsorption of 1,1,1-trichloroethane on uranium dioxide produced a series of Type II adsorption isotherms. These isotherms, shown in Fig. 4, were obtained from three or more runs and typify multilayer adsorption. The experiments indicate that there was no chemical reaction between the solvent and the oxide. The adsorption isotherms were reversible although the time required to reach equilibrium was greater during desorption.

Previous adsorption of solvents on ura-

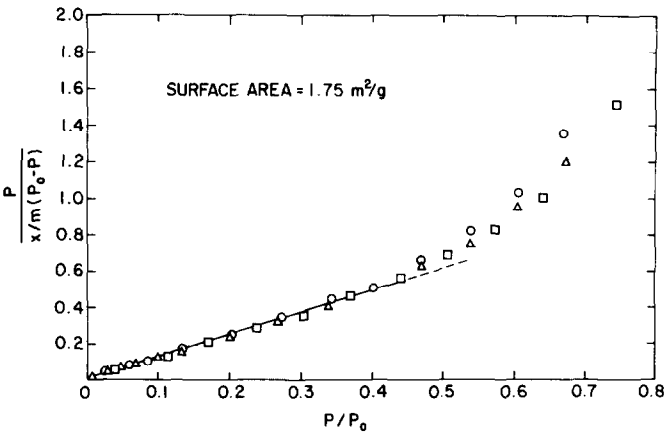

FIG. 3. BET plot of the argon adsorption data.

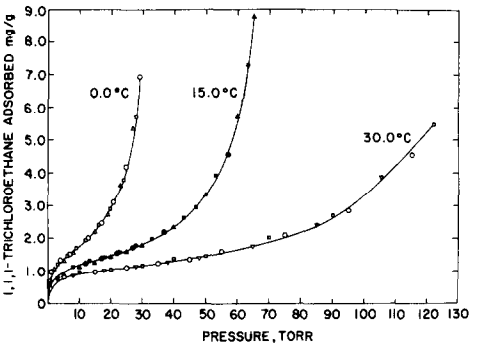

FIG. 4. Isotherms for the adsorption of 1,1,1-trichloroethane on uranium dioxide. Symbols denote multiple adsorption runs at each temperature.

nium dioxide indicated the oxide surface was heterogeneous and the data at all temperatures readily fit the Freundlich equation (*1,2*). Application of the Freundlich equation to the data from this experiment was satisfactory only at 0 and 15°C.

Molecular Area of 1,1,1-Trichloroethane

The foundation for the most universally accepted method of calculating the surface area of powders was laid by Brunauer, Emmett and Teller (*4*). Their equation,

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C}\frac{P}{P_0}, \quad (1)$$

was derived for volumetric adsorption measurements where V is the volume of gas adsorbed and V_m is the volume of gas required to form an adsorbed monolayer. If for gravimetric adsorption studies the weight of the adsorbed gas is substituted for the volume, the modified BET equation becomes

$$\frac{P}{(x/m)(P_0 - P)} = \frac{1}{(x/m)_m C} + \frac{C-1}{(x/m)_m C}\frac{P}{P_0}, \quad (2)$$

where x/m is the weight of adsorbed gas and $(x/m)_m$ is the weight of a monolayer. Application of Eq. (2) is generally valid if the isotherms are Type II with well-defined "knee-bends" or plateau regions.

The Type II isotherms obtained for CH_3CCl_3 adsorption on UO_2 were evaluated using the BET equation. Figure 5 shows a least squares fit of the data at 0.0, 15.0, and 30.0°C. Table 1 summarizes the BET constants obtained for both argon and CH_3CCl_3 adsorption.

The principal application of the BET equation is the calculation of adsorbent surface areas. Through use of a *standard* adsorbent, however, the molecular area, ω, of any new adsorbate may be calculated.

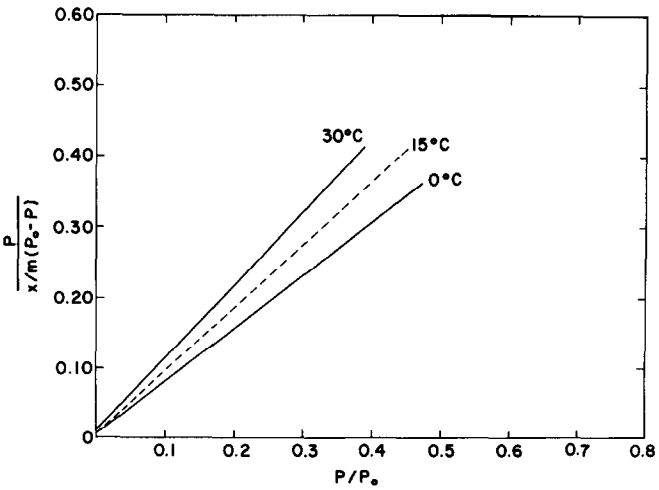

FIG. 5. BET plots of the 1,1,1-trichloroethane adsorption data at 0.0, 15.0, and 30.0°C.

TABLE 1
BET CONSTANTS FOR ARGON AND 1,1,1-TRICHLOROETHANE ADSORPTION ON UO_2

Adsorbate	Temp (°C)	$(x/m)_m$ (mg/g)	c(BET)
Argon	−197.7	0.81	278
1,1,1-Trichloroethane	0.0	1.40	45
	15.0	1.16	58
	30.0	0.99	89

Assuming the UO_2 surface area measured by the adsorption of argon is correct, the apparent molecular area of CH_3CCl_3 may be calculated by the equation

$$\omega = 13.8 \frac{(x/m)_m^{Ar}}{(x/m)_m^{CH_3CCl_3}}, \quad (3)$$

where $(x/m)_m^{Ar}$ is the BET monolayer capacity for argon adsorbed on the UO_2 and $(x/m)_m^{CH_3CCl_3}$ is the BET monolayer capacity for CH_3CCl_3. Using Eq. (3) and the BET constants obtained at 0.0, 15.0, and 30.0°C, the average value for ω for 1,1,1-trichloroethane was 33 ± 5 Å.

The validity of this number may be suspect since the value of ω depends on the nature of the adsorbent. To provide a check on this method of determining molecular areas, a second method was also employed. If it is assumed that the molecules adsorbed on the surface have the same packing as those in the condensed phase, the value of ω is given by

$$\omega = 3.464 \times 10^{16} \left[\frac{M}{4\sqrt{2}\, N\delta_1}\right]^{2/3}, \quad (4)$$

where M is the molecular weight, N is Avogadro's number, and δ_1 is the liquid density of the adsorbate (*5*). Using this equation ω for CH_3CCl_3 was calculated to be 32.7 Å^2. The agreement between the two methods of calculating ω is very good. This suggests that there is relatively weak localization of the adsorbed CH_3CCl_3 molecules which corresponds to continuous molecular layers.

Potential Theory of Adsorption

Polanyi's theory (*5–7*) defines the adsorption potential at a point near the adsorbent surface as the work done by the temperature independent adsorption forces in bringing a molecule from the gas phase to that point near the surface. The potential theory applies to both monomolecular and multimolecular adsorption. The function of this theory is to determine the distribution of the volume of adsorption space, ϕ, as a function of the adsorption potential ϵ. That is,

$$\phi = f(\epsilon), \quad (5)$$

which is the equation of the characteristic curve. The adsorption potential is determined by the equation,

$$\epsilon = RT \ln P_0/P_x, \quad (6)$$

where P_x is the equilibrium pressure and P_0 is the vapor pressure. In Polanyi's concept of equipotential surfaces, the volume enclosed between the adsorbent and the equipotential surface of potential ϵ is ϕ and is given by

$$\phi = \frac{x/m}{\delta_T}. \quad (7)$$

In this equation, x/m is the weight of the adsorbed film and δ_T is the liquid density at the adsorption temperature T.

Figure 6 shows the characteristic curve for the adsorption of CH_3CCl_3. This curve was calculated from the adsorption isotherms discussed earlier. The temperature independence is illustrated by the fact that the points from all three isotherms fall on the single characteristic curve.

For adsorbents which are either nonporous or contain large pores Dubinin (*8*) has shown that the equation for the characteristic curve can be written as

$$\phi = \phi_0 e^{-m\epsilon/\beta}, \quad (8)$$

or

$$\log \phi = \log \phi_0 - 0.434 \frac{m\epsilon}{\beta}, \quad (9)$$

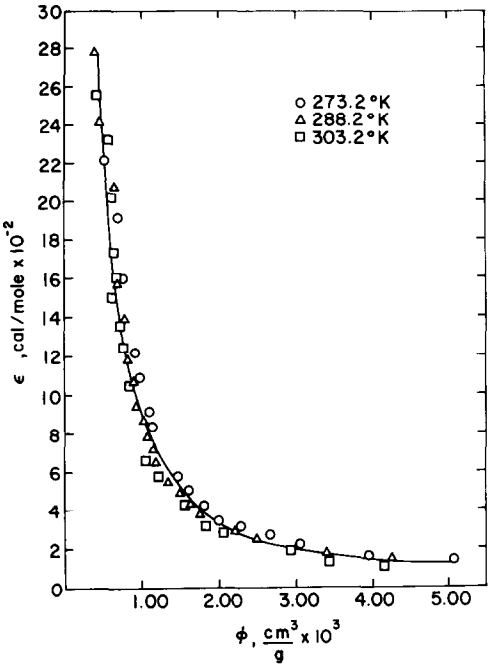

FIG. 6. Polanyi characteristic curve for the adsorption of 1,1,1-trichloroethane on uranium dioxide.

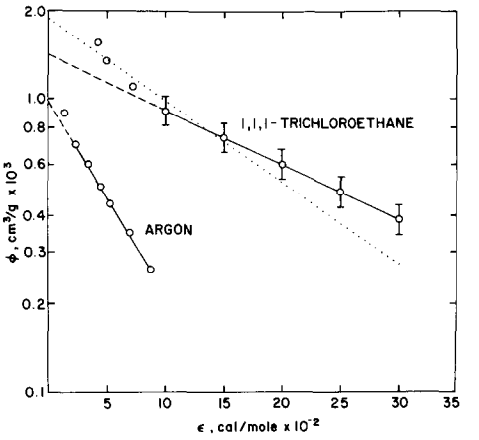

FIG. 7. Dubinin–Polanyi characteristic curve for argon and 1,1,1-trichloroethane adsorption on uranium dioxide. The dotted curve associated with the 1,1,1-trichloroethane is the theoretical curve calculated from trichloroethylene adsorption data.

where ϕ_0 is the limiting volume of adsorption space, m is a structural constant for the adsorbent, and β is the affinity coefficient for the adsorbate. For the same adsorbent the limit volume ϕ and the structural constant m should be constant and independent of the adsorbate. The affinity coefficient β, however, does vary with the adsorbate. Dubinin and Timofeyev (*9*) have shown that β can be closely expressed by the ratio of the molar volume of the adsorbate to the molar volume of reference compound, in this case benzene. Therefore, for CH_3CCl_3

$$\beta = \frac{V_{CH_3CCl_3}}{V_{benzene}} = 1.11. \qquad (10)$$

From the adsorption of trichloroethylene on uranium dioxide (*2*) it was determined that the limit volume ϕ was 0.0019 cm³/g and the value for the structural constant m was 7×10^{-4}. Using these adsorbent constants as well as the calculated value of 1.11 for the affinity coefficient β for CH_3CCl_3 a theoretical characteristic curve was calculated from Eq. (9).

Figure 7 shows both the experimental and the theoretical curve for CH_3CCl_3. Using a least-squares computer fit of the data the limit volume was found to be 0.0014 cm³/g compared to the theoretical value of 0.0019 cm³/g determined from the trichloroethylene data. Also included in Fig. 7 is the characteristic curve for argon which produced a limit volume of 0.0010 cm³/g. The difference in the limit volume for argon, trichloroethylene, and 1,1,1-trichloroethane could be due to experimental variations or the use of adsorption data instead of desorption data. Reucroft *et al.* (*10*) found that desorption data were more reproducible and resulted in a more linear characteristic curve.

Heat of Adsorption

The isosteric heat of adsorption of CH_3CCl_3 was calculated from the adsorption isotherms using the Clausius-Clapeyron equation (*11*). These heats were found to be independent of temperature as indicated by the linear adsorption isosteres shown in Fig. 8. The variation of the isosteric heat of adsorption with surface cover-

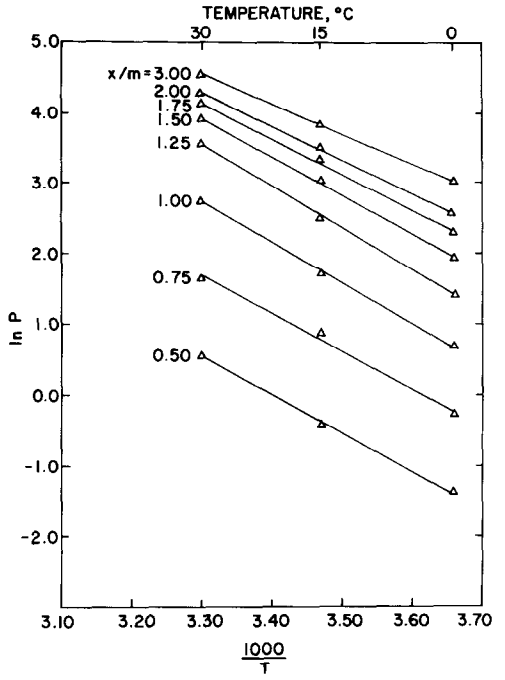

FIG. 8. Adsorption isosteres for 1,1,1-trichloroethane adsorption on uranium dioxide.

age is shown in Fig. 9. For surface coverages less than one monolayer the variation of the heat of adsorption was complex and difficult to explain. A similar type of behavior was observed by Orr (*12*) for the adsorption of argon on potassium chloride and by Beebe and Young (*13*) for the adsorption of argon on carbon black. In these cases the increase in the heat of adsorption between $\Theta = 0$ and $\Theta = 1$ was attributed to the attraction between the adsorbed argon atoms. Another factor which could contribute to the complexity of the heat curve is the heterogeneity of the surface.

Beginning at $\Theta = 1$ the heat of adsorption decreased with increasing coverage to approach a limiting value of 7.7 kcal/mole which is the heat of vaporization (*14*). The total decrease in the heat of adsorption during multilayer adsorption was from 12 kcal/mole to about 8 kcal/mole.

CONCLUSION

The interaction between uranium dioxide and 1,1,1-trichloroethane was studied using a series of adsorption measurements in the temperature range 0–30°C. Adsorption was found to be physical in nature and was evaluated using both the BET equation and the potential theory of adsorption. Calculations of the isosteric heat of adsorption revealed a complex variation of the heat of adsorption with surface coverage. Values for the isosteric heat of adsorption varied from 12 to 8 kcal/mole. The uranium dioxide surface area, as measured by argon adsorption, was used to calculate the molecular area of

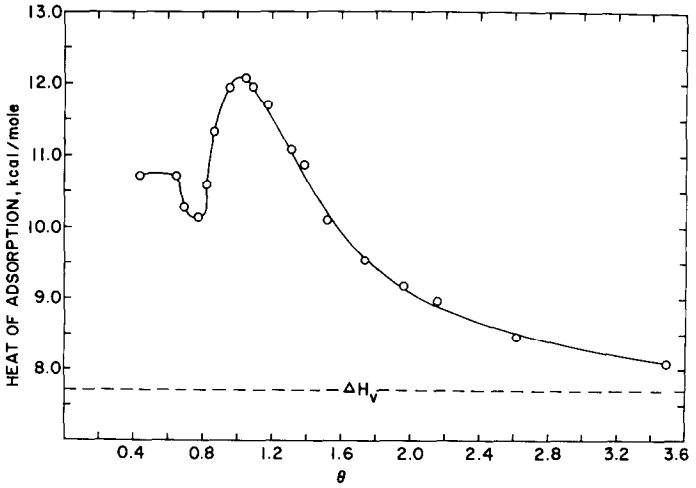

FIG. 9. Variation of the isosteric heat of adsorption with surface coverage.

CH_3CCl_3. This resulted in a value of 33 ± 5 Å^2 compared to a theoretical value calculated to be 32.7 Å.

ACKNOWLEDGMENT

The assistance of Mr. Douglas M. Adams in making the experimental measurements is gratefully acknowledged.

REFERENCES

1. Stakebake, J. L., and Goad, H. A., *J. Catal.* **32,** 272 (1974).
2. Stakebake, J. L., *J. Catal.* **35,** 153 (1974).
3. DeBoer, J. H., *in* "Surface Area Determination" (D. H. Everett and R. H. Ottewill, Eds.) p. 7. Butterworth, London, 1970.
4. Brunauer, S., Emmett, P. H., and Teller, E., *J. Amer. Chem. Soc.* **60,** 309 (1938).
5. Brunauer, S., "The Adsorption of Gases and Vapors." Princeton Univ. Press, Princeton, NJ, 1943.
6. Knowles, A. J., and Moffat, J. B., *J. Colloid. Interface Sci.* **41,** 116 (1972).
7. Polanyi, M., *Trans. Faraday Soc.* **28,** 316 (1932).
8. Dubinin, M. M., *Chem. Rev.* **60,** 235 (1960).
9. Dubinin, M. M., and Timofeyev, D. P., *C. R. Acad. Sci. URSS* **54,** 701 (1946).
10. Reucroft, P. J., Simpson, W. H., and Jonas, L. A., *J. Phys. Chem.* **75,** 3526 (1971).
11. Stakebake, J. L., *J. Nucl. Mater.* **23,** 154 (1967).
12. Orr, W. J. C., *Trans. Faraday Soc.* **35,** 1247 (1939).
13. Beebe, R. A., and Young, D. M., *J. Phys. Chem.* **58,** 93 (1954).
14. Riddick, J. A., and Bunger, W. B., "Techniques of Chemistry," Vol. 2, p. 357. Wiley (Interscience), New York, 1970.