

$\times 10^{-10}$ for phenylmercuric hydroxide, 1.5×10^{-5} for phenylmercuric acetate, and 3.1×10^{-5} for phenylmercuric propionate. Each of these values was found to be constant for experimental points taken over a wide range of ($T_{\text{acid}}/T_{\text{PhHgOH}}$) values. The constant for the hydroxide is further substantiated since it was used in calculating both of the other constants. The value for phenylmercuric hydroxide found in the present work agrees with the value of 1.0×10^{-10} that has been reported.² These constants may be used in estimations of equilibrium constants for the interaction of phenylmercury compounds with groups such as the sulphydryl group in biological materials.

SORPTION OF SULFUR HEXAFLUORIDE BY ARTIFICIAL ZEOLITES

By DANIEL BERG AND WILLIAM M. HICKAM

Westinghouse Central Laboratories, Pittsburgh 35, Pennsylvania

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The small and uniform size of the intracrystalline pores left by the removal of water from hydrated crystalline zeolites results in "molecular sieve" action. Molecules of large diameter are excluded from the pores; smaller diameter molecules may be sorbed in the intracrystalline pores. With mixtures of molecules of diameter smaller than the sieve pore sizes preferential sorption may take place.

Habgood¹ has studied the kinetics of Molecular Sieve action for nitrogen-methane mixtures. In this case nitrogen diffuses more rapidly into the small pores and is preferentially taken up in the early stages of sorption but methane has a higher affinity for the sieve and is preferentially sorbed at equilibrium.

In this work we are interested in studying the sorption of a molecule of roughly 5 Å. diameter, namely, SF_6 , as a function of temperature and pressure and the selective sorption in mixtures of SF_6 and air.

Experimental Procedure

A gas circulatory system with mass spectrometer² was used in measuring sorption of SF_6 by the Molecular Sieve. This system offers several advantages over other equipment used for similar measurements. The calibrated volume and manometer permits accurate determination of the quantity of gas used. The system is attached to the mass spectrometer which provides analysis of the gas when desired. When mixtures of gases are being used the circulating pump ensures that the gas above the sieve is of uniform composition. This condition, combined with the mass spectrometric analysis, permits calculation of the quantity of each component adsorbed even though there are large temperature gradients in the system due to heating of the sieve.

A weighed amount of sieve was placed in the system. The sieve was evacuated and heated to about 200° to remove adsorbed gases. Sulfur hexafluoride was introduced at known pressure in the known volume of the gas circulatory system which was isolated from the sieve. When the SF_6 was exposed to the sieve the pressure dropped immediately and the sieve became heated. The procedure of filling the reservoir to a known pressure of SF_6 and then opening the sieve to the reservoir was repeated sev-

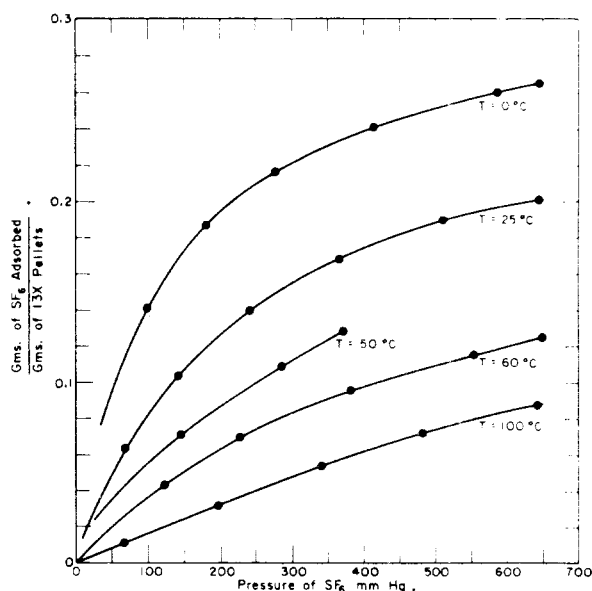


Fig. 1.—Adsorption of SF_6 on #13X Molecular Sieve pellets as a function of temperature and pressure.

eral times till the desired equilibrium pressure and temperature were reached. Knowledge of the system volume and pressure and the gas composition allowed the weight of SF_6 adsorbed on the sieve to be calculated for each final pressure above the sieve. The procedure was repeated with the sieve at equilibrium temperatures ranging from 0 to 100°. The reversibility of the adsorption also was established by evacuating measured quantities of SF_6 from the reservoir and then allowing the sieve to come to equilibrium temperature and pressure.

Sulfur hexafluoride from General Chemical Co., Pittsburgh, Pa., of greater than 99% purity was used. Mass spectrometrically identified tank impurities found were O_2 , N_2 , A, CF_4 , and H_2O . With the exception of water and slight amounts of nitrogen the impurities are not sorbed by the Molecular Sieve at room temperature and higher.

There are four pore size sieves of Molecular Sieve available from the Linde Co., Tonawanda, N.Y. These include the 4A type of about 4 Å. pore width, 5A type to approximately 5.1 Å. pore width, 10X of about 10 Å. and 13X type of roughly 13 Å. pore width. They are synthetic alkali metal aluminosilicates. Both powder and 3.2 mm. pellets were used. The pellets are made by binding the powder with an inert clay-type binder amounting to 20% of the total weight of the pellet. Some of the properties of the 4A synthetic zeolites have been described by Breck, Eversole, Milton, Reed and Thomas³ and the crystal structure has been determined by Reed and Breck.⁴

Results and Discussion

The results of the sorption of pure SF_6 on type 13X Molecular Sieve are shown in Fig. 1 where the grams of SF_6 sorbed per gram of pellet is plotted as a function of the pressure of SF_6 for various Molecular Sieve temperatures. It should be remembered that the pellets contain 20% of inert clay binder. The true sorption fractions are 20% higher than graphed. This was confirmed by measuring pure 13X powder in a similar experiment. Type 10X gives similar curves. Both the 4A and 5A Molecular Sieve sorb less than 0.01 g. of SF_6 for each gram of pellet at 25° and 1 atmosphere.

From a plot of the pressure of SF_6 above the

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(3) D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Reed and T. L. Thomas, *J. Am. Chem. Soc.*, **78**, 5963 (1956).

(4) T. B. Reed and D. W. Breck, *ibid.*, **78**, 5972 (1956).

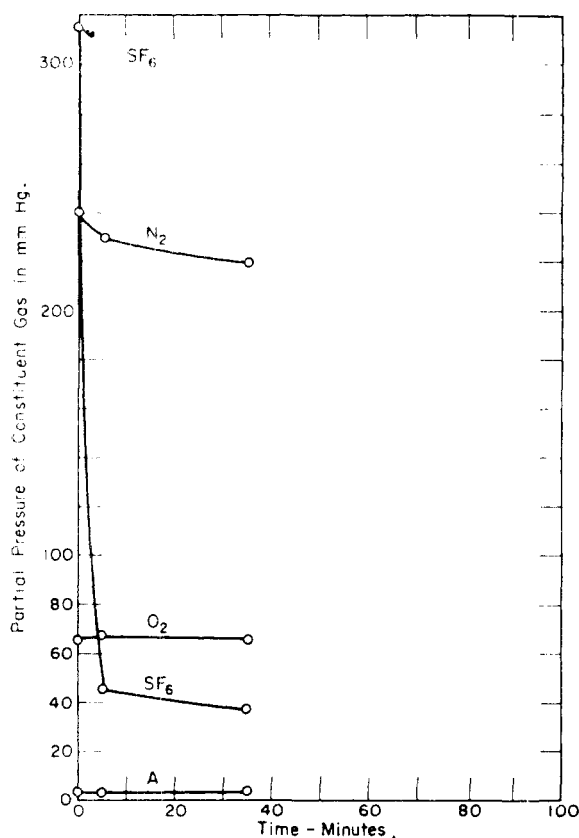


Fig. 2.—Adsorption of SF_6 from an air- SF_6 mixture by 13X sieve at 25° .

sieve against the reciprocal absolute temperature for various per cent. by weight adsorbed SF_6 one can determine the heat of adsorption by means of the equation

$$\log \frac{P_2}{P_1} = \frac{\Delta H}{2.3R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

In this equation ΔH is the heat of adsorption (cal./mole), R is a constant equal to 2 cal./degree-mole, and P_1, P_2, T_1, T_2 are the respective pressures and absolute temperatures. From such a plot ΔH was calculated to be about 5 kcal./mole. This means that heat is given off when the SF_6 is adsorbed and conversely heat is required to desorb the SF_6 . The heat of sublimation of SF_6 is 5.64 kcal./mole at -64° .⁵ The value of 5 kcal./mole is typical for physical adsorption.

The diameter of SF_6 calculated from the S-F distance of 1.58 Å.,⁶ the F tetrahedral covalent radius of 0.7 Å. and the less probable F^- ionic radius of 1.4 Å.⁷ leads to a value of 3.86 to 4.56 Å., both of which are smaller than the requisite 5 Å. size for the 5A Molecular Sieve. Using the relationship derived from kinetic theory,⁸ $\eta = 0.499\rho\bar{v}L$ where ρ is the density, \bar{v} the average velocity and L the mean free path, it is found that the cross-section calculated from the viscosity η is 6.4 Å. Apparently SF_6 is too large to penetrate the pores

of the Molecular Sieve with 5 Å. diameter or smaller pores. It is clear that the diameter computed from the ionic and/or covalent bond radii is not the correct one to use. It is more appropriate to use the cross-section computed from kinetic theory which considers the collision size and not the electron cloud size.

It should be noted that not only is the size of the molecule important from the standpoint of getting into the pores of the sieve, but it is necessary for the molecule to be adsorbed on the surface of the sieve. The adsorption on the surface depends on the magnitude of the interaction of the molecule with the surface. Since dipole-dipole interaction may be large, polar molecules interact with the polar surface of the sieve to a large extent, so that, if the polar molecule is small enough, a large quantity will be adsorbed. Non-polar molecules which may possess a quadrupole moment are adsorbed by the molecule being polarized by the surface of the sieve (a weak dipole is induced in the non-polar molecule by the polar surface of the sieve). If the non-polar molecule is small enough to enter the pores of the sieve and if the polarizability of the molecule in one direction is sufficient to have a large enough dipole induced in the non-polar molecule, the non-polar molecule will be adsorbed. In this qualitative discussion we are assuming that the temperature is constant because it is really the ratio of the energy of interaction of the molecule (polar or non-polar) and the surface to the thermal energy of the gaseous molecules (of the order of kT) which is important, as well as the size of the pores and molecules. SF_6 has a polarizability of 16.51⁹ which is almost 4 times that of oxygen or nitrogen and would be expected to physisorb more readily than O_2 or N_2 . The larger interaction energy of the SF_6 molecule with the surface of the sieve as compared to that between SF_6 molecules makes it possible to obtain adsorption of the SF_6 above the critical temperature of SF_6 (46°). For example, at 60° and 1 atmosphere pressure, the sieve adsorbs about 15% by weight of SF_6 . Assuming a surface area of 800 meters²/g.¹⁰ and using the thickness of the adsorbed monolayer of SF_6 as 6 Å. the calculated volume of SF_6 adsorbed on the surface of one gram of sieve is about 0.5 cm.³. Hence, the density of the adsorbed 0.15 g. of SF_6 in a volume of 0.5 cm.³ at 60° would be 0.3 g./cm.³. This compares to a liquid density of 0.73 g./cm.³ at the critical point.¹¹ A rough general rule is that the higher the value of the critical temperature of the gas the more the gas will be adsorbed at any temperature if the pores are larger than the molecules. The general rule is understandable if it is recalled that, above the critical temperature, a gas cannot be liquefied no matter what the pressure, and that the critical temperature gives a measure of the interaction of the molecules of the gas.

Additional experiments were performed with known mixtures of SF_6 and air. In Fig. 2 are

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shown curves illustrating the selective adsorption of SF_6 from a 50% air and 50% SF_6 mixture. The SF_6 adsorption characteristics of the sieve are found to be independent of the air concentration. The SF_6 commercially available contains impurities of CF_4 , O_2 , N_2 , A and H_2O . With the exception of water, and slight amounts of nitrogen, the other impurities are not adsorbed by the sieve and thus this provides a means for purifying SF_6 . Mild heating removes the SF_6 and not the water. The SF_6 interacts through an induced dipole whereas water adsorbs by dipolar interaction.

THE HEAT OF FORMATION OF CF_2

BY LEO BREWER, JOHN L. MARGRAVE,¹ RICHARD F. PORTER
AND KARL WIELAND

Department of Chemistry, University of California, Berkeley, California
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Available data for the heat of formation of CF_2 are based on the general analogy of the C-F system with the C-H system² or on rates of reaction of Na with fluorinated methanes,³ and suggest $\Delta H_f^\circ \leq -18$ kcal./mole. No lower limit on the heat has been suggested. Margrave⁴ has concluded recently from a mass spectrometric study of C_2F_4 and the appearance potential of CF_2^+ that $\Delta H_f^\circ \approx -30 \pm 10$ kcal./mole.

Further evidence regarding CF_2 has been deduced by determining the lowest temperature at which CF_2 bands may be detected in absorption in the system CF_4 -graphite.⁵ The first faint, but clearly visible bands (2487 and 2457 Å.) appear at 1830°K. from the reaction $\text{CF}_4(\text{g}) + \text{C}(\text{s}) = 2\text{CF}_2(\text{g})$ with $P_{\text{CF}_4} = 0.18$ atm. From the very diffuse nature of the bands, it is likely that a minimum of 0.0015 mm. of CF_2 at 1800°K. is required for detection, while the maximum amount is probably 0.015 mm. at 1800°K., depending on the transition probability. These pressures, along with the known heat of formation of $\text{CF}_4(\text{g})$,⁶ and other standard thermodynamic functions, lead one to calculate $\Delta H_f^\circ(\text{CF}_2) \leq -30$ kcal./mole at 298°K.

A comparison also can be made with the Si-Cl system for which Schafer and Nickl⁷ have reported the heat of formation of the analogous molecule SiCl_2 as -30 kcal./mole. One can compare the heat of atomization of SiCl_2 (192 kcal./mole) with the heat of atomization of SiCl_4 (365 kcal./mole) and establish the ratio

$$\frac{\Delta H_a(\text{MX}_2)}{\Delta H_a(\text{MX}_4) - \Delta H_a(\text{MX}_2)} = 1.11$$

A similar value for this ratio appears to hold for the Si-F system.⁸ If exactly the same ratio holds

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- (6) C. A. Neugebauer and J. L. Margrave, *J. Phys. Chem.*, **60**, 1318 (1956).
- (7) H. Schafer and J. Nickl, *Z. anorg. u. allgem. Chem.*, **274**, 250 (1953).
- (8) A. Kanaan and J. L. Margrave, unpublished work, University of Wisconsin 1961.

for the C-F system, $\Delta H_a(\text{CF}_2) = 243$ kcal./mole and $\Delta H_f^\circ(\text{CF}_2) = -36$ kcal./mole.

Thus, it appears that the heat of formation of $\text{CF}_2(\text{g})$ is considerably more negative than previously thought with the correct value in the range -35 ± 10 kcal./mole.

REACTION OF ATOMIC HYDROGEN WITH SOLIDS AT -195° ¹

BY VINCENT J. DECARLO AND F. O. RICE

Department of Chemistry, Georgetown University, Washington 7, D. C.
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This work was started with the idea of synthesizing LiH_3 . The fundamental notion is that negative ions tend to grow in order to give more room for the electronic cloud and consequently one might expect, given proper conditions, that the proton in lithium hydride could incorporate two hydrogen atoms to form the ion H_3^- . The method used was that developed by Klein and Scheer² in which hydrogen atoms react with various substances frozen on a liquid nitrogen-cooled surface. Our results (largely negative) are shown in Table I.

TABLE I
ACTION OF ATOMIC HYDROGEN ON VARIOUS SUBSTANCES
UNDER VARIOUS TEMPERATURES

Substance	Temp., °C.	Results
Li	-195	No reaction
Li	100	Fast reaction
Na, Hg, Cd, Mg		
Zn, Bi, Ge, Ga	-195	No reaction
Ca	-195	Very slow reaction
Ba	-195	H atoms go to H_2 which is absorbed. No further reactions
	100	
Cu	-195	Apparently an unstable hydride first forms and then decomposes as concn. increases
HN_3	-195	Very slow reaction
HN_3	-150	Very slow reaction
COS	-195	Very slow reaction
Acetic anhydride	-195	No reaction
<i>n</i> -Butylamine	-195	No reaction
Isobutylamine	-195	No reaction
Ethyl alcohol	-195	No reaction
Amyl alcohol	-195	No reaction
Acetone	-195	Very slow reaction
<i>n</i> -Propyl alcohol	-195	Very slow reaction
Carbon tetrachloride	-195	Very slow reaction
Isobutyl alcohol	-195	Slow reaction
<i>sec</i> -Butyl alcohol	-195	Slow reaction
<i>t</i> -Butyl alcohol	-195	Slow reaction
<i>n</i> -Butyl alcohol	-195	Slow reaction (faster than the three previous)
Ethyl iodide	-195	Fast reaction

To our very great surprise, ethyl iodide reacts readily with hydrogen atoms at -195° ; the white solid turns orange and gives a positive test for free iodine using starch indicator. We positively

- (1) Presented at the Fifth International Symposium on Free Radicals, Uppsala, Sweden, July, 1961.
- (2) R. Klein and M. D. Scheer, *J. Phys. Chem.*, **62**, 1011 (1958).