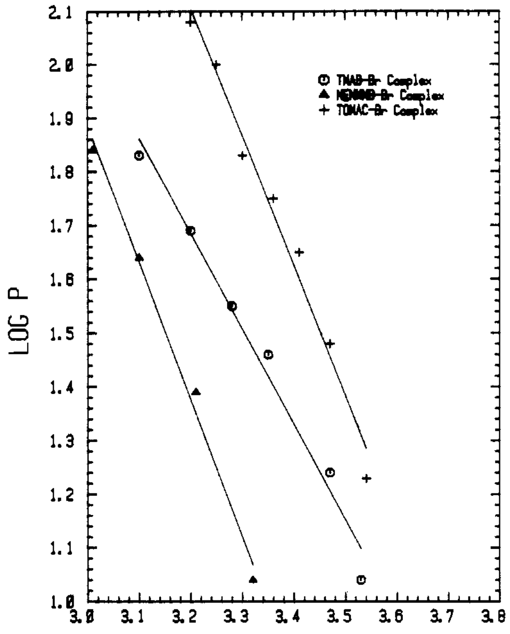

Figure 3. Vapor pressures of bromine–quaternary ammonium salt complexes.

III. The data are also plotted in Figure 2 together with bromine vapor-pressure data reported by Weast (*3*). The data show that, at a given temperature, vapor pressures follow the order bromine > TOMAC–Br > TMAB–Br > NENMMB–Br. This illustrates that complexing of bromine with quaternary ammonium salts reduces the concentration of bromine vapor over the complex surfaces.

The integrated Clausius–Clapeyron equation relates vapor pressure to temperature:

$$\log P = -0.434(\Delta H_v/R)(1/T) + \text{constant} \qquad (1)$$

where P is the pressure in mmHg, T is the temperature in Kelvin, R is the universal gas constant, and ΔH_v is the molar heat of vaporization. The value of the constant depends in part on the units used for pressure. The vapor-pressure data for the three bromine complexes are replotted in Figure 3, which shows that the log P vs. $1/T$ relationship for the three bromine complexes is linear.

The best-fit lines to represent the vapor pressure–temperature relationship for a complex and the calculated molar heat of vaporization are as follows:

(1) TMAB–Br complex

$$\log P = (-2.184 \times 10^3)(1/T) + 8.692 \qquad (2)$$

The coefficient of determination for the calculated line is 0.927. ΔH_v = 9.996 kcal/mol.

(2) NENMMB–Br complex

$$\log P = (-2.551 \times 10^3)(1/T) + 9.544 \qquad (3)$$

The coefficient of determination for the calcualted line is 0.990. ΔH_v = 11.67 kcal/mol.

(3) TOMAC–Br complex

$$\log P = (-3.675 \times 10^3)(1/T) + (1.402 \times 10^1) \qquad (4)$$

The coefficient of determination for the calculated line is 0.881. ΔH_v = 16.82 kcal/mol. In eq 2–4, pressure is given in mmHg, and temperatures in Kelvin. The heat of vaporization for the TMAB–Br complex, 9.996 kcal/mol of bromine, is in reasonably good agreement with approximately 11 kcal/mol reported by Bloch et al. (*2*).

Acknowledgment

Thanks are due to Dr. Robert G. Zalosh for his thoughtful comments on this paper and to Mr. Roy Tsui for assistance in fabricating the apparatus.

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Received for review April 10, 1980. Accepted August 15, 1980. Financial Support of Electric Power Research Institute (EPRI), Palo Alto, CA, is gratefully acknowledged.

Sorption of SF_6 by Activated Charcoal

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Sorption isotherms for SF_6 on activated charcoal were obtained between −83 and 100 °C in the pressure range of 0.13 mPa to 100 kPa (1 μtorr to 750 torr) by microgravimetric techniques. Charcoal uptakes as high as 0.80 g of SF_6 per gram of charcoal were observed with isosteric heats of sorption values ranging from −6.0 to −7.5 kcal/(g-mol).

Introduction and Background

Sulfur hexafluoride (SF_6) is an important gaseous dielectric, with significant utility in the electric power industry. This gas possesses a high dielectric strength, about twice that of air or carbon dioxide, and has excellent arc quenching characteristics due to the rapid recombination of dissociated molecules and a large electron attachment cross section (~0.48 nm). The latter property permits the absorbed electron energy to be stored in the vibrational levels of the SF_6 molecules and the formation of stable negative ions of low mobility. The removal of free electrons through the formation of negative ions makes it possible to achieve higher voltage levels before an arc across the potential gradient between surfaces is produced. In addition, considerable decomposition may occur in the SF_6 without significant loss of dielectric strength.

As a consequence of these properties, SF_6 is used as an insulating gas in high-voltage transformers, circuit breakers and waveguides, and linear and electrostatic accelerators. Large quantities are used in the latter applications. For example, the

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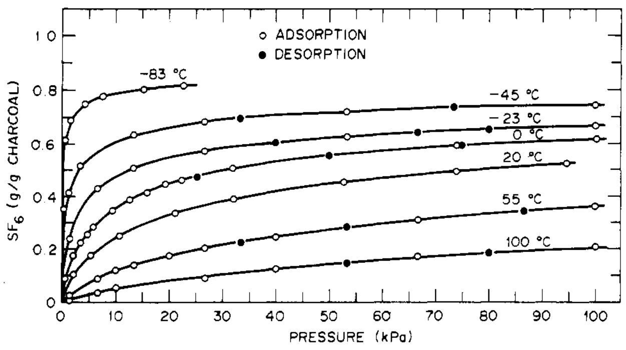

Figure 1. SF_6 loading isotherms on activated charcoal.

large electrostatic accelerator at the Holifield Heavy Ion Facility of the Oak Ridge National Laboratory (*1*) is contained in a vessel filled with ~100 Mg of SF_6 at ~590 kPa (5.8 atm). When it is necessary to remove the SF_6 from the accelerator vessel, it is transferred to storage vessels and contained as a liquid at ambient temperature at ~2.41 MPa (23.8 atm) pressure. As a result of repeated transfers of this type, the concentration of air in the SF_6 will increase to a level that will require purification of the SF_6. This is needed primarily to minimize the storage volume that will accommodate the contents of the accelerator vessel when the SF_6 is liquefied at ambient temperature for storage. An examination of various purification processes was presented by Perona and Watson (*2*). They also discussed SF_6 purification by adsorption on activated carbon based on earlier studies by Brassard (*3*).

The use of packed-bed columns of activated carbon has been proposed as an effective and convenient way to separate SF_6 from air and other low-boiling-point contaminants. When a mixture of SF_6 and air is passed through such a column at a temperature in the range -50 to 0 °C, SF_6 is selectively adsorbed until the column is saturated. After breakthrough, the sorbed SF_6 can be recovered by warming the bed or by reducing the pressure or by both. A good understanding of the SF_6 sorption and desorption processes on activated carbon is required to design these columns effectively and to select the best operating conditions. In this communication, experimental data pertinent to the design of such systems, namely, the sorption isotherms and isosteric heats of sorption for SF_6 on activated carbon for the temperature range of -83 to 100 °C and for the pressure range of 0.13 mPa to 100 kPa (1 μtorr to 750 torr), are presented.

The only related work on SF_6 sorption on carbonaceous materials appeared to be by Beebe et al. (*4*, *5*). However, their work was conducted by using nonporous graphitized carbon black, so that their findings do not bear directly on the results presented here.

Experimental Section

An activated carbon sample (Fisher Scientific Co. activated cocoanut charcoal 6-14 mesh, 5-685-A) was placed into the environmental chamber of a Cahn RG vacuum electrobalance (*6*, *7*) and outgassed overnight at room temperature (21 °C) to 0.13 mPa (1 μtorr). The sample weight was continuously monitored by a strip recorder.

As a basis for comparison with subsequent SF_6 runs, the N_2 sorption isotherm at -196 °C was determined first. This proved to be a type-I isotherm without hysteresis (*8*) because of the microporosity of the charcoal (*9*). The calculated BET area was 957 m^2/g, a typical value for microporous materials. The ultimate N_2 uptake was ~0.45 g per gram of charcoal at a P/P_0 value of 1. Following the N_2 sorption studies, the charcoal was restored to its original weight by outgassing to 0.13 mPa (1 μtorr) at room temperature, and the SF_6 (Matheson Instrument Grade 99.99% pure) experiments were initiated. The isotherms were determined at temperatures of -83, -45, -23, 0, 20, 55, and 100 °C, but no sorption experiments were made at pressures greater than 100 kPa (750 torr) to prevent damage to the vacuum equipment.

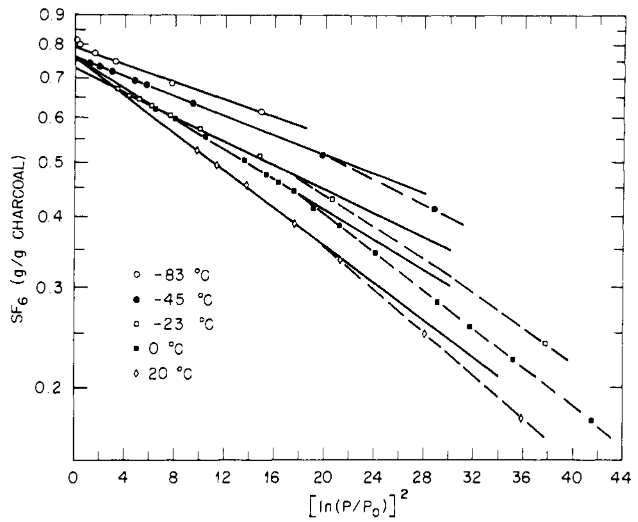

Figure 2. Dibinin-Raduskevich plots for the SF_6 sorption on activated charcoal.

Table I. Properties of SF_6 and Activated Charcoal

temp, °C	vapor pressure (P_0),[a] kPa	liquid SF_6 density,[a] g/cm³	Γ_0, (g of SF_6)/(g of C)	micropore vol, cm³/(g of C)
-83	25	2.00	0.79	0.40
-45	285	1.82	0.76	0.42
-23	625	1.71	0.73	0.43
0	1260	1.56	0.76	0.49
20	2130	1.39	0.76	0.55

[a] Data taken from ref *11*.

Results and Discussion

The SF_6 isotherms (Figure 1) all conformed to the type-I classification. It should be noted that for the -83 °C isotherm, the P/P_0 value of 1 is reached at 25 kPa without any significant increase in SF_6 uptake. This result, which is in agreement with the N_2 sorption data, indicated that the activated charcoal is microporous. This is further substantiated by the absence of measurable hysteresis throughout the $P-T$ range investigated.

The SF_6 isotherm data were also analyzed according to the following Dubinin-Raduskevich (D-R) equation (*10*):

$$\ln \frac{\Gamma}{\Gamma_0} = -D\left(\ln \frac{P}{P_0}\right)^2 \qquad (1)$$

where Γ is the amount of SF_6 sorbed in grams of SF_6 per gram of charcoal when the relative pressure is P/P_0, Γ_0 is the total amount sorbed at $P/P_0 = 1$, and D is a D-R constant. Therefore, for temperatures less than 45.6 °C (critical temperature of SF_6), a semilogarithmic plot of SF_6 loading, Γ, as a function of $(\ln P/P_0)^2$ should be linear with an intercept of Γ_0 (Figure 2). A least-squares fit of the experimental data for $(\ln P/P_0)^2$ over the linear region ($(\ln P/P_0)^2 < 18$) gave intercepts, Γ_0, equivalent to the sorption of between 0.73 and 0.79 g of SF_6 per gram of charcoal. Total micropore volumes for the activated charcoal were calculated as a function of temperature from the corresponding values of Γ_0 and the liquid SF_6 densities (Table I). The micropore volumes, which are typical for microporous solids, ranged from 0.40 to 0.55 cm³ per gram of

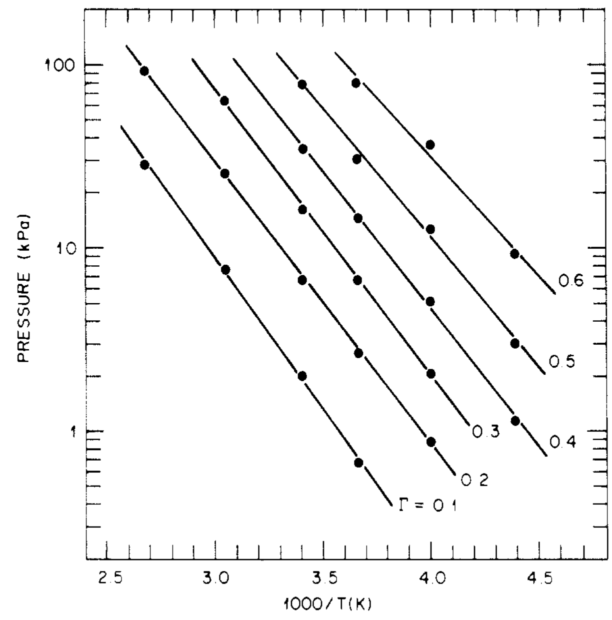

Figure 3. SF_6 adsorption isosteres on activated charcoal.

charcoal as the temperature increased from -83 to 20 °C (Table I). The nonlinearity of the experimental data for abscissa values greater than ~18 is shown by the dashed lines in Figure 2. The upward turn of the -83 °C isotherm in Figure 2 as P/P_0 approached 1 can be explained in terms of multilayer adsorption on the external surface of the charcoal.

The amount of heat released on adsorption is an important parameter in designing packed-bed sorption columns. Unless this heat is removed effectively, the efficiency of SF_6 sorption will be severely diminished (*2*). The various isotherms (Figure 1) also provide implicit information on the differential isosteric heats of sorption according to the following Clausius-Clapeyron equation:

$$\left(\frac{\partial \ln P}{\partial T}\right)_{\Gamma} = -\frac{Q_{\mathrm{iso}}}{RT^2} \qquad (2)$$

When eq 2 is evaluated at a fixed Γ (i.e., at a constant uptake), an isosteric heat of sorption (Q_{iso}) may be calculated for that particular value of Γ.

The P-T relations for the SF_6 sorption process on activated charcoal were determined by applying the integrated form of eq 2 to data taken from Figure 1. Plots of ln P vs. $1/T$ for several values of SF_6 sorption (Γ) were linear as shown by the least-squares fit to the data points in Figure 3. Correlation coefficients, which were in the range 0.999-0.993, decreased with increasing SF_6 sorption. The slopes of the isosteres are proportional to Q_{iso}/R; therefore, isosteric heats of sorption, Q_{iso}, were calculated as a function of SF_6 sorption (Figure 4). Values of Q_{iso} first decreased as SF_6 sorption increased, leveled off briefly around -7 kcal/(g-mol of SF_6), and then decreased more rapidly to a value approaching the latent heat of condensation of SF_6, ~-4 kcal/(g-mol of SF_6). This behavior conformed to the general characteristics of gas sorption on activated carbon as reported previously (*10*).

The sorption isotherms for nitrogen and water vapor are given in Figure 5, presented in terms of the liquid volume equivalent in each case. Thus we note that these smaller molecules gain access to the internal volume (ca. 0.6 mL/g) accessible to SF_6 only at higher temperatures (see Table I). The truly carbonaceous nature (nonoxidized) is noted in the hydrophobic character of the water isotherm (Figure 5) (*12*). These results also show that sorption of sulfur hexafluoride will not be markedly hindered by sorbed water as long as the relative humidity is kept appreciably below ~50%.

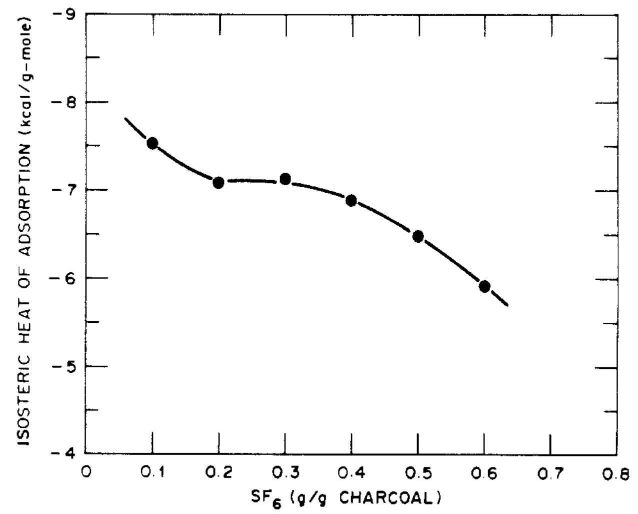

Figure 4. Isosteric heat of adsorption of SF_6 on activated charcoal.

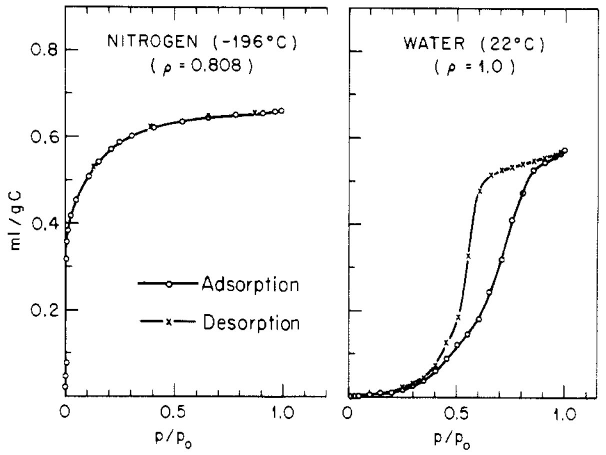

Figure 5. Sorption isotherms for nitrogen and water on activated charcoal.

Acknowledgment

We gratefully acknowledge the contributions of D. O. Williams, M. F. Couturier, B. V. Hu, and R. E. Piret of the Massachusetts Institute of Technology, School of Chemical Engineering Practice, at Oak Ridge National Laboratory.

Glossary

P	pressure, Pa
P_0	saturation pressure, Pa
Q_{iso}	isosteric heat of adsorption, kcal/(g-mol)
R	ideal gas constant, 1.987 cal/(K g-mol)
T	temperature, K
Γ	amount sorbed, g of SF_6/g of charcoal, $< P/P_0 <$ 1
Γ_0	amount sorbed, g of SF_6/g of charcoal, $P/P_0 = 1$

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Received for review April 24, 1980. Accepted September 9, 1980. This research was sponsored by the Office of Basic Energy Sciences, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corp.

Dissociation Constants of Diethanolamine and Diisopropanolamine in an Aqueous 1.00 M Potassium Chloride Solution

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The dissociation constants of diethanolamine (DEA) and diisopropanolamine (DIPA) have been determined potentiometrically in an aqueous potassium chloride solution (1.00 M) at 293, 303, 313, and 323 K. Their dissociation constants were shown to be identical, within experimental error, and can be expressed at zero ionic strength ($I = 0$) by the equation $\log K_{I=0} = (-1.82 \times 10^3)/T - 4.10 + (4.44 \times 10^{-3})T$.

Table I. Dissociation Constants for DEA and Commercial-Grade DIPA in 1.00 M Potassium Chloride Solution[a]

	10^9K, mol/L			
T, K	293	303	313	323
DIPA commercial grade	0.512	0.914	1.62	3.01
	0.534	0.915	1.63	2.79
DEA	0.527	0.957	1.67	2.94
	0.538	0.951	1.59	2.88

[a] $K = m_{H^+}m_{Am}/m_{AmH^+}$; m_i = concentration of component i.

Introduction

Alkanolamines are frequently used to remove acidic components (e.g., H_2S and CO_2) from natural and refinery gases. The most important alkanolamines for this operation are monoethanolamine (MEA), diethanolamine (DEA), and diisopropanolamine (DIPA) (*3*), and they are usually employed in aqueous solution. For some applications, however, a combined solvent is more efficient (e.g., water and sulfolane in the "Sulfinol" process (*2*)).

The capabilities of the various amines in the absorption of acidic gases depend on, among other factors, their dissociation constants. The dissociation constant of DIPA has been reported only once, but this value (pK = 9.5 at 298 K (*6*)) differs considerably more from those of DEA (pK = 8.88 at 298 K (*4*)) and isopropanolethanolamine (IPEA, pK = 8.81 at 298 K (*4*)) than can be expected on basis of the closely resembling molecular structures. The reported dissociation constant of the secondary amine DIPA is even very similar to that recorded for MEA, a primary amine (pK = 9.498 at 298 K (*4*)).

Therefore the main aim of the present investigation was to provide reliable dissociation constants for DIPA at several temperatures (293, 303, 313, and 323 K). Further, as commercial grade DIPA contains small amounts of monoisopropanolamine (MIPA), the dissociation constants obtained for both commercial grade and pure DIPA were compared.

Experimental Section

Chemicals. Aqueous hydrochloric acid and sodium hydroxide solutions were prepared from Merck Titrisol ampules and potassium chloride (Merck analytical-grade reagent). Carbon dioxide-free double-distilled water was used throughout.

The amines were analyzed by gas chromatography (*5*): DEA (UCB) was 98.5% pure on a water-free basis and pure DIPA (99.9%) was obtained by vacuum distillation of commercial-grade (BASF) DIPA (99.0%).

Procedure. The dissociation constants were determined at constant ionic strength in aqueous 1.00 M potassium chloride solutions, at least in duplicate, as follows. Samples of the aqueous amine solutions (±0.1 M, 4 and 6 mL) were blanketed with nitrogen, acidified with an excess of aqueous hydrochloric acid (0.1000 M, 8 mL) to prevent absorption of carbon dioxide, and finally diluted to 50 mL with potassium chloride (1.00 M).

The protonated amine, acting as a weak acid, and the excess of hydrochloric acid were titrated in a thermostatically controlled vessel with an aqueous sodium hydroxide solution (0.1000 M). The titration was followed potentiometrically by using a Knick industrial pH meter (type DIN) and a Schott combined glass-calomel electrode (type N) with a platinum-wire diaphragm. The method used for calibration of the electrode is identical with that used by Bos (*1*).

The data from the titration curve were used to calculate the excess of hydrochloric acid, the amount of protonated amine, and the dissociation constant of the amine by means of the multiparameter curve-fitting procedure described by Bos (*1*). The sum of excess hydrochloric acid and the amount of protonated amine was found to be within 1% of the total quantity of hydrochloric acid initially added.

Results and Discussion

Two series of experiments were performed. In the first series the dissociation constants of DEA and commercial-grade DIPA were compared at 293, 303, 313, and 323 K (Table I). From these results it can be concluded that at 1.00 M ionic

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