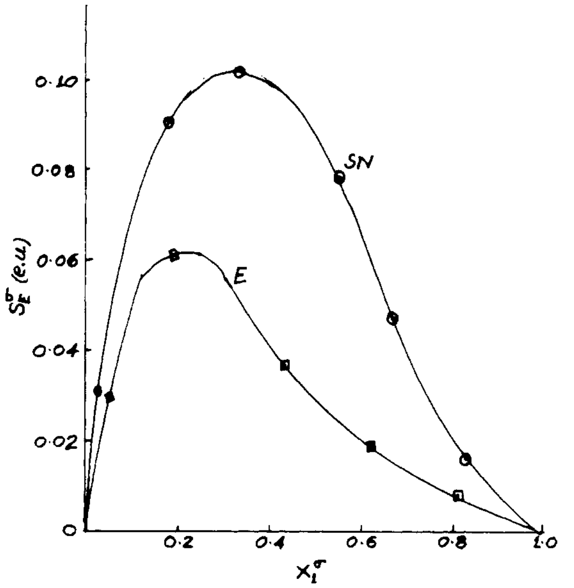

Figure 5. Excess surface entropy (S_E^σ) vs. surface mole fraction (x^σ) of benzene–dioxane on alumina.

therefore, reduces simply to $-R\sum x_i^\sigma \ln \rho_i^\sigma$ and, when plotted as a function of composition (x_i^σ), should yield a simple curve with one maximum. The curves obtained according to the S_E^σ values of two models are shown in Figure 5. Although the actual values from the two models are different, the natures of the curves are similar.

Conclusion

The adsorption of both benzene–cyclohexane and benzene–dioxane solutions decreases with a rise in the temperature range from 20 to 40 °C. This effect is more pronounced (~5 times) in benzene–dioxane than in benzene–cyclohexane. Benzene–cyclohexane solutions show multilayer adsorption. The surface activity coefficients are independent of temperature in this temperature range.

Glossary

σ	surface phase
l	bulk liquid
i	component 1
j	component 2
n_0	total amount of liquid mixture
Δx_i^l	change in mole fraction due to adsorption
m	mass of the solid
a	thermodynamic activity
S	specific surface area of solid
A	surface area of adsorbate
S_E^σ	excess surface entropy
T	temperature
R	gas constant
E	Everett's model
SN	Schay and Nagy's model
ρ^σ	surface activity coefficient
x^σ	surface mole fraction
γ	surface tension

Registry No. Alumina, 1344-28-1; benzene, 71-43-2; cyclohexane, 110-82-7; dioxane, 123-91-1.

Literature Cited

(1) Kipling, J. J. "Adsorption from Solutions of Non-electrolytes"; Academic Press: London, 1969.
(2) Schay, G.; Nagy, L. G.; Szekrenyesy, T. *Period. Polytech.* **1962**, *6*, 91–7.
(3) Suri, S. K.; Ramakrishna, V. *Trans. Faraday Soc.* **1969**, *65*, 1960–4.
(4) Everett, D. H. *Trans. Faraday Soc.* **1964**, *60*, 1803–13.
(5) Patel, M.; Ramakrishna, V. *J. Colloid Interface Sci.* **1980**, *76*, 166–73.
(6) Suri, S. K.; Patel, M. *J. Colloid Interface Sci.* **1981**, *84*, 36–41.
(7) Eriksson, J. C. *Ark. Kemi* **1966**, *25*, 331–41.
(8) Patel, M.; Ramakrishna, V. *J. Colloid Interface Sci.* **1982**, *85*, 284–8.

Received for review August 6, 1982. Revised manuscript received March 26, 1984. Accepted April 30, 1984. We are thankful to the Director, Indian Institute of Technology, New Delhi, and to the Director, Council of Scientific and Industrial Research, New Delhi, for their financial support.

Measurement of the Volumetric Properties of Sulfur Hexafluoride from 260 to 340 K at Pressures to 2.5 MPa

Jørgen Mollerup

Instituttet for Kemiteknik, Danmarks Tekniske Højskole, Bygning 229, 2800 Lyngby, Danmark

The volumetric properties of sulfur hexafluoride are determined experimentally by a Burnett apparatus at 260, 285, 315, and 340 K at pressures to 2.5 MPa. Compression factors are calculated by fitting simultaneously the isothermal pressure series to the Burnett relation and the virial equation. The calculated second virial coefficients agree well with available data from the literature. Densities and compression factors at integral pressures are calculated from the experimental data. The purity of the gas is 99.7%.

Burnett Apparatus

The gas-phase *PVT* properties are obtained by the Burnett method (*1*) in which only temperature and pressure measurements are required. The apparatus is identical with the one described by Fredenslund et al. (*2*) and Mollerup and Angelo (*3*). The Burnett cell consists of two thick-walled vessels of unspecified volume, here approximately 125 and 275 cm^3, connected to each other by means of an expansion valve. The Burnett cell is located in a thermostat and the larger volume connected to the pressure measuring system by means of a diaphragm differential pressure indicator. The pressure is measured on either an oil dead-weight piston gauge or an air dead-weight piston gauge depending upon the pressure range.

The larger vessel in the Burnett apparatus is evacuated and filled with the gas or gas mixture to be studied, and the smaller vessel is evacuated and kept under high vacuum. After isothermal conditions are obtained, the temperature and pressure are measured. The valve on the vent line to the vacuum system is closed and the expansion valve is then opened, and the pressure is allowed to equalize between the two vessels. The temperature and pressure are measured again after isothermal

0021-9568/85/1730-0021$01.50/0

Table I. Experimental Pressures, Calculated Residuals, and Compression Factors of Sulfur Hexafluoride at 260, 285, 315, and 340 K

P^*, MPa	$P^* - P$, MPa	Z
	T = 260 K	
0.546 655 7	0.000 004	0.895 76
0.400 375 1	0.000 032	0.925 98
0.290 235 3	0.000 028	0.947 48
0.208 861 9	−0.000 050	0.962 75
0.149 686 6	0.000 016	0.973 59
0.106 868 3	−0.000 003	0.981 28
0.076 135 16	0.000 001 1	0.986 73
0.054 153 50	0.000 004 9	0.990 60
0.038 429 66	−0.000 038 1	0.993 34
0.027 298 16	−0.000 007 7	0.995 28
0.658 746 3	−0.000 048	0.871 05
0.486 745 1	0.000 016	0.908 39
0.354 930 7	0.000 017	0.934 97
0.256 580 8	0.000 060	0.953 86
0.184 293 1	0.000 004	0.967 28
0.131 835 2	−0.000 010	0.976 80
0.094 024 23	−0.000 027 5	0.983 56
0.066 925 14	−0.000 030 4	0.988 35
0.779 662 5	0.000 021	0.842 58
0.582 207 2	0.000 037	0.888 09
0.427 392 0	−0.000 109	0.920 52
0.310 440 6	−0.000 015	0.943 60
0.223 798 3	0.000 034	0.959 99
0.160 417 7	−0.000 030	0.971 63
0.114 616 7	−0.000 019	0.979 89
0.081 715 51	0.000 016 3	0.985 75
0.058 164 69	0.000 040 9	0.989 90
0.041 318 15	0.000 017 9	0.992 84
0.029 358 69	0.000 038 0	0.994 93
	T = 285 K	
0.794 745 1	0.000 055	0.887 18
0.583 538 7	0.000 048	0.919 55
0.423 775 2	0.000 011	0.942 74
0.305 469 6	0.000 006	0.959 31
0.219 013 2	−0.000 035	0.971 11
0.156 501 3	−0.000 011	0.979 50
0.111 525 9	−0.000 020	0.985 46
1.139 260	0.000 097	0.829 02
0.854 289 2	−0.000 004	0.877 64
0.629 340 4	−0.000 005	0.912 70
0.458 081 2	−0.000 023	0.937 84
0.330 719 9	−0.000 013	0.955 81
0.237 431 4	0.000 005	0.968 62
0.169 763 9	−0.000 008	0.977 73
0.121 066 2	0.000 005	0.984 20
1.538 104	−0.000 026	0.748 88
1.192 117	0.000 017	0.819 33
0.897 209 8	−0.000 124	0.870 62
0.662 629 7	−0.000 066	0.907 65
0.483 195 9	0.000 004	0.934 23
0.349 264 9	0.000 015	0.953 23
0.250 972 0	0.000 051	0.966 78
0.179 526 2	0.000 004	0.976 43
0.128 086 9	0.000 023	0.983 28

P^*, MPa	$P^* - P$, MPa	Z
	T = 315 K	
1.710 358	−0.000 553	0.818 56
1.287 402	−0.000 147	0.869 20
0.951 257 8	−0.000 065	0.906 19
0.694 187 5	0.000 068	0.932 96
0.502 065 7	−0.000 007	0.952 21
0.360 944 9	−0.000 025	0.965 99
0.258 445 8	0.000 021	0.975 83
0.184 435 4	−0.000 026	0.982 83
0.131 633 9	0.000 243	0.987 82
1.421 269	0.000 067	0.853 76
1.055 902	0.000 089	0.894 96
0.773 331 8	0.000 081	0.924 85
0.560 847 4	0.000 082	0.946 39
0.403 872 2	−0.000 026	0.961 83
0.289 464 6	−0.000 062	0.972 86
0.206 782 6	−0.000 063	0.980 72
0.147 408 2	−0.000 020	0.986 31
1.359 757	−0.000 054	0.860 91
1.007 713	0.000 070	0.900 17
0.736 742 0	0.000 055	0.928 61
0.533 633 5	0.000 029	0.949 09
0.383 992 5	−0.000 019	0.963 76
0.275 097 9	−0.000 010	0.974 24
0.196 462 3	−0.000 001	0.981 70
0.139 941 7	−0.000 045	0.987 01
2.288 660	0.000 222	0.738 72
1.778 256	−0.000 010	0.809 98
1.342 709	0.000 116	0.862 90
0.994 273 9	0.000 086	0.901 61
0.726 566 8	0.000 067	0.929 66
0.526 070 4	0.000 021	0.949 84
0.378 482 1	−0.000 004	0.964 30
0.271 051 3	−0.000 054	0.974 62
0.193 561 2	−0.000 021	0.981 97
0.137 851 6	−0.000 072	0.987 20
0.098 043 44	−0.000 071 1	0.990 92
0.069 725 67	0.000 006 5	0.993 56
0.049 540 69	0.000 037 5	0.995 43
0.035 211 63	0.000 081 8	0.996 76
0.024 961 67	0.000 041 5	0.997 71

P^*, MPa	$P^* - P$, MPa	Z
	T = 340 K	
2.521 419	0.000 175	0.792 29
1.913 437	0.000 545	0.848 32
1.422 850	0.000 362	0.890 26
1.043 110	0.000 215	0.921 10
0.756 855 9	−0.000 125	0.943 52
0.545 516 4	−0.000 072	0.959 70
0.391 211 3	−0.000 065	0.971 30
0.279 565 7	−0.000 058	0.979 59
0.199 236 0	−0.000 101	0.985 50
0.141 816 5	−0.000 036	0.989 71
0.100 807 0	−0.000 013	0.992 70
0.071 616 05	0.000 022 4	0.994 82
0.050 817 47	0.000 009 6	0.996 33
0.036 101 65	0.000 060 7	0.997 40
1.841 862	0.000 230	0.854 57
1.366 705	0.000 166	0.894 89
1.000 393	0.000 044	0.924 48
0.725 250 7	−0.000 068	0.945 97
0.522 276 3	−0.000 096	0.961 45
0.374 485 0	0.000 059	0.972 55
0.267 371 5	−0.000 110	0.980 49
0.190 625 1	−0.000 004	0.986 14
2.055 568	−0.000 399	0.835 57
1.535 674	−0.000 031	0.880 80
1.129 498	0.000 054	0.914 18
0.821 616 3	−0.000 004	0.938 51
0.593 218 0	0.000 116	0.956 09
0.425 901 7	0.000 082	0.968 71
0.304 584 8	0.000 037	0.977 75
0.217 108 3	−0.000 115	0.984 19
1.544 284	−0.000 258	0.880 05
1.136 046	−0.000 179	0.913 64
0.826 677 6	−0.000 020	0.938 12
0.596 841 5	0.000 000	0.955 81
0.428 691 6	0.000 150	0.968 51
0.306 723 9	0.000 210	0.977 60
0.218 804 4	0.000 169	0.984 08

conditions are obtained, which generally takes 2–3 h depending on how pronounced the Joule–Thomson effect is. The expansion valve is then closed, and the smaller volume evacuated. These expansions are continued until a low pressure is reached.

Reduction of Burnett Data

The result of the experiment is a series of decreasing pressures P_1, P_2, ..., P_i, ..., P_I at constant temperature. It was shown by Burnett that the pressures from an expansion series must satisfy the relation

$$Z_i/Z_1 = (P_i/P_1)N^{i-1} \qquad (1)$$

where N is the apparatus constant defined as

$$N = (V_a + V_b)/V_a \qquad (2)$$

Several schemes for least-squares reduction of Burnett data are possible. In this work we have applied the method of Dalton et al. (*4*), but replaced the Newton–Raphson optimization routine by a Levenberg–Marquardt routine.

It is assumed that the experimental data are subject to random errors only and that the virial equation is able to accurately represent the isothermal compression factors as a function of density. Furthermore, the apparatus constant must be independent of pressure; otherwise an explicit expression for the pressure dependence must be known. In this work we have neglected the pressure dependence of the apparatus constant as discussed elsewhere by Mollerup and Angelo (*3*).

Several isothermal expansion series can be reduced simultaneously. If we denote the number of expansion series by M, and the number of expansions in series m by Im, then series

Table II. Parameters Determined by a Least-Squares Fit of the Experimental Pressures to the Objective Function

	parameter	std error
	T = 260 K	
N	1.41152972	1.2×10^{-4}
B_1, L/mol	$-3.72145275 \times 10^{-1}$	3.2×10^{-3}
B_2, (L/mol)^2	$1.02311881 \times 10^{-2}$	5.3×10^{-3}
	T = 285 K	
N	1.41165616	6.3×10^{-5}
B_1, L/mol	$-3.05221560 \times 10^{-1}$	7.9×10^{-4}
B_2, (L/mol)^2	$1.78882606 \times 10^{-2}$	7.1×10^{-4}
	T = 315 K	
N	1.41103060	9.4×10^{-5}
B_1, L/mol	$-2.40756177 \times 10^{-1}$	1.0×10^{-3}
B_2, (L/mol)^2	$1.67925246 \times 10^{-2}$	7.0×10^{-4}
	T = 340 K	
N	1.41123823	9.8×10^{-5}
B_1, L/mol	$-2.03868896 \times 10^{-1}$	1.0×10^{-3}
B_2, (L/mol)^2	$1.71894819 \times 10^{-2}$	7.4×10^{-4}

m contains the pressures P^*_{1m}, P^*_{2m}, ..., P^*_{Im}.

The densities are calculated by minimizing the residual sum of squares

$$F = \sum_{m=1}^{M} (\sum_{i=1}^{I} w_i (P^*_i - P_i)^2)_m \qquad (3)$$

where P^*_i is the experimental pressure and P_i the calculated pressure that must satisfy the Burnett relation eq 1, that is

$$P_{im} = (Z_{im}/Z_{1m}) P_{1m} N^{1-im} \qquad (4)$$

The compression factor $Z = P/(\rho RT)$ is calculated from the virial equation of state

$$Z_{im} = 1 + \sum_{j=1}^{J} B_j \rho^j_{im} \qquad (5)$$

The parameters in the least-squares data reduction procedure are the virial coefficients B_j and if desired the apparatus constant N and the initial pressures P_{1m}. If the initial pressures P_{1m} are not parameters to be estimated, they are assumed to be exact and thus $P_{1m} = P^*_{1m}$.

The weight factor w_i is a function of the observed pressure

$$w_i = 1/\sum(a_j + b_j P_i)^2 \qquad (6)$$

where a_j and b_j are constants that depend on the barometer, the differential pressure indicators, and the dead-weight gauge used.

Results and Discussion

The application of sulfur hexafluoride to high-voltage CGI problems requires accurate measurements of the volumetric properties of sulfur hexafluoride (*5*). Table I shows the experimental pressures of sulfur hexafluoride and the calculated residuals and compression factors. The compression factors are calculated from eq 5 at pressures that satisfy the Burnett relation eq 1. They are not calculated at the experimental pressures P^*.

The parameters and the standard errors of the parameters are shown in Table II. The first parameter is the apparatus constant of approximately 1.4; the other parameters are virial coefficients. Table III shows a comparison of calculated second virial coefficients and the smooth numbers from Dymond and Smith (*6*); the agreement is generally very good.

Table III. Second Virial Coefficients

	second virial coeff, cm^3/mol	
T, K	this work	ref *6*
260	−372.1 ± 3	−380 ± 8
285	−305.2 ± 0.8	−310.8 ± 6
315	−240.8 ± 1	−244.9 ± 5
340	−203.9 ± 1	−203.4 ± 5

Table IV. Interpolated Densities and Compression Factors

P, MPa	ρ, mol/L	Z
	T = 260 K	
0.1	0.047 083	0.9825
0.2	0.095 935	0.9644
0.3	0.146 76	0.9456
0.4	0.199 81	0.9261
0.5	0.255 40	0.9056
0.6	0.313 91	0.8842
0.7	0.375 84	0.8616
0.8	0.441 84	0.8376
	T = 285 K	
0.1	0.042 758	0.9870
0.2	0.086 685	0.9737
0.3	0.131 87	0.9601
0.4	0.178 42	0.9461
0.5	0.226 45	0.9318
0.6	0.276 10	0.9171
0.7	0.327 52	0.9020
0.8	0.380 91	0.8863
0.9	0.436 47	0.8702
1.0	0.494 48	0.8535
1.5	0.835 79	0.7574
	T = 315 K	
0.1	0.038 539	0.9908
0.2	0.077 814	0.9814
0.3	0.117 86	0.9719
0.4	0.158 73	0.9622
0.5	0.200 45	0.9524
0.6	0.243 08	0.9425
0.7	0.286 66	0.9324
0.8	0.331 27	0.9221
0.9	0.376 95	0.9116
1.0	0.423 78	0.9010
1.5	0.678 25	0.8444
2.0	0.978 37	0.7805
	T = 340 K	
0.1	0.035 633	0.9928
0.2	0.071 794	0.9855
0.3	0.108 50	0.9781
0.4	0.145 78	0.9707
0.5	0.183 64	0.9631
0.6	0.222 12	0.9556
0.7	0.261 23	0.9479
0.8	0.301 00	0.9402
0.9	0.341 46	0.9324
1.0	0.382 63	0.9245
1.5	0.600 39	0.8838
2.0	0.841 67	0.8406
2.5	1.113 4	0.7943

Table IV shows calculated densities and compression factors at integral pressures.

The experimental error of the measured compression factors is estimated to be 0.1% or less and to be mainly due to the uncertainty in the temperature and pressure. The absolute error in the temperature is less than 0.03 K at the triple point of water.

Acknowledgment

I am grateful to Bent Johnsen, who assisted with the experiments.

Registry No. Sulfur hexafluoride, 2551-62-4.

Literature Cited

(1) Burnett, E. S. *J. Appl. Mech. Trans.* **1936**, *A146*, 58.

(2) Fredenslund, Aa.; Mollerup, J.; Christiansen, L. J. *Cryogenics* **1973**, *13*, 414–9.

(3) Mollerup, J.; Angelo, P. *Fluid Phase Equilib.*, in press.

(4) Dalton, B. J.; Moffitt, R. L.; Barleau, R. E.; Smith, D. R. "A General Computer Program for Use in Reduction of Burnett Compressibility Data"; U.S. Department of the Interior, Bureau of Mines: Washington, DC, 1970; Inf. Circ.-U.S., Bur. Mines No. 8491.

(5) Vibholm, S.; Mollerup, J., presented at the 6th International Conference on Gas Discharges and Their Applications, Edinburgh, September 8–11, 1980, IEE Conf. Publ. No. 189.

(6) Dymond, J. H.; Smith, E. B. "The Virial Coefficients of Pure Gases and Mixtures", Clarendon Press; Oxford, 1980.

Received for review April 2, 1984. Accepted August 7, 1984.