

SURFACE TENSION AND COEXISTENCE CURVE OF SULPHUR-HEXAFLUORIDE UP TO THE CRITICAL POINT

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Tension superficielle et courbe de coexistence de l'hexafluorure de soufre des basses températures jusqu'au point critique

RÉSUMÉ : *Dans la thermodynamique phénoménologique et statistique de la transition de phase on prête une attention particulière à la prévision de la tension superficielle et à la forme de la courbe de coexistence. La comparaison de la théorie avec l'expérience souffre du manque de bonnes données expérimentales en particulier sur la tension superficielle pour un domaine de températures étendu.*

Dans ce rapport on présente les valeurs de la tension superficielle de l'hexafluorure de soufre sous deux phases en équilibre des basses températures jusqu'au point critique. On les obtient en mesurant la différence d'élévation capillaire dans quatre capillaires de diamètres différents. On détermine la différence de densité entre liquide et vapeur qui est nécessaire pour calculer la tension superficielle à l'aide de mesures de l'indice de réfraction en utilisant la relation de Lorentz-Lorenz.

On présente l'influence de la température sur la tension superficielle et la courbe de coexistence dans une équation empirique dont les constantes et les exposants sont comparés avec les nouvelles formules, présentées récemment, du principe des états correspondants et les valeurs obtenues par calcul statistique.

The surface tension σ and coexistence curve $(\rho_l - \rho_v)$ have been measured from 3°C up to the critical point. The results may be represented by $\sigma = \sigma_0 (1 - T/T_c)^n$ with $\sigma_0 = 55.31$ dyn/cm, $n = 1.286$ and $(\rho_l - \rho_v) = \rho_c B_0 (1 - T/T_c)^\beta$ with $B_0 = 3.86$ and $\beta = 0.342$, $T_c = 318.63$ K.

Surface tension is of particular interest in boiling problems as well as in the theoretical treatment of phase transition. Numerous equations describing the temperature dependence of the surface tension of a liquid have been proposed [1, 2, 3, 4]. But inspection of the literature made it apparent that large gaps exist in accurate experimental data ranging from low temperatures up to the critical point. The primary object of our investigations is to fill some of these gaps.

The liquid-vapour density differences $\rho_l - \rho_v$ are needed to compute the surface tension, we therefore have determined these values simultaneously by refractive index measurements. Sulfur hexafluoride (SF₆) has been chosen as a first test fluid due to its symmetrical shape and high molecular weight ($M = 146$ g/moles) which makes it of theoretical interest in the study of intermolecular forces. Moreover, SF₆ has some possibilities as a refrigerant.

EXPERIMENTAL METHOD

The surface tension is measured by the method proposed by Sugden [5], in which the vertical distance h between the free liquid surfaces in two capillary tubes with different radii r_i is measured, a third and fourth tube were added as a check. Primarily from the measurements of h_{12} , h_{13} etc. one obtains the capillary constants a_{12}^2 , a_{13}^2 etc.:

$$a_{12}^2 = h_{12} / (1/b_1 - 1/b_2) \quad (1)$$

where h_{12} is the difference between the lowest points of each meniscus in tubes 1 and 2, b_1, b_2 are the radii of curvature at these points. Sugden's table was used for the calculation of the meniscus corrections. It could be assumed that the liquid SF₆ wetted the glass, i.e. that the contact angle of the liquid with glass was zero [10]. The surface tension σ is evaluated from the equation

$$\sigma = a_{12}^2 \cdot g \cdot (\rho_l - \rho_v) / 2 \quad (2)$$

where g is the acceleration due to gravity.

In order to avoid additional uncertainties due to inaccurate density data the term $\rho_l - \rho_v$ was determined by measurements of the refractive index n applying the Lorentz-Lorenz function

$$\frac{n^2 - 1}{n^2 + 2} \frac{1}{\rho} = R \quad (3)$$

For a homogeneous, nonpolar medium the specific refraction R can be assumed as a constant, [6, 7, 8, 9]. An average value may be determined in a temperature range where reliable density data are available. The actual values of $\rho_l - \rho_v$ are then to be evaluated from

$$(\rho_l - \rho_v) = \left[\left(\frac{n^2 - 1}{n^2 + 2} \right)_l - \left(\frac{n^2 - 1}{n^2 + 2} \right)_v \right] / R \quad (4)$$

Figure 1 shows schematically the arrangement of the capillaries and the prism inside the sample vessel. Particular attention has been paid to the calibration of the capillary tubes, the radii of which have been determined to (in mm) $r_1 = 0.07636$, $r_2 = 0.12445$, $r_3 = 0.24194$, $r_4 = 0.32177$, $r_5 = 0.05109$ (used in a second run). The capillary rise of the liquid inside a tube was measured by means of a kathetometer to within ± 0.005 mm.

The optical measurements were made with a mercury vapour lamp, wave length $\lambda = 5.461 \cdot 10^{-5}$ cm, illuminating an adjustable slit on a collimating telescope used as a light source. The prism inside the sample cell was adjusted to the optical axis of the arrangement by means of an auto-collimating telescope which was equally applied to observe the angle of refraction in conjunction with a Deckel optical circular table. The uncertainty of the reading was less than $\pm 4''$.

The primary element used for temperature measurements was a Pt-100 platinum resistance thermometer (absolute accuracy ± 0.02 K).

Sulfur hexafluoride is stated to be 99.95% SF₆, the principle impurities being air (0.02%), CF₄ (0.02%) and H₂O (6 ppm.)

RESULTS

Coexistence curve: The following equations representing the coexistence curve have been obtained by refractive index measurements

$$\left(\frac{n^2 - 1}{n^2 + 2} \right)_l - \left(\frac{n^2 - 1}{n^2 + 2} \right)_v = (0.2215 \pm 0.00065) (1 - T/T_c)^{(0.3422 \pm 0.0006)} \quad (5)$$

the rectilinear diameter:

$$\left[\left(\frac{n^2 - 1}{n^2 + 2} \right)_l + \left(\frac{n^2 - 1}{n^2 + 2} \right)_v \right] / 2 = (10.564 \pm 0.02) \cdot 10^{-2} - (4.836 \pm 0.012) \cdot 10^{-2} T/T_c \quad (6)$$

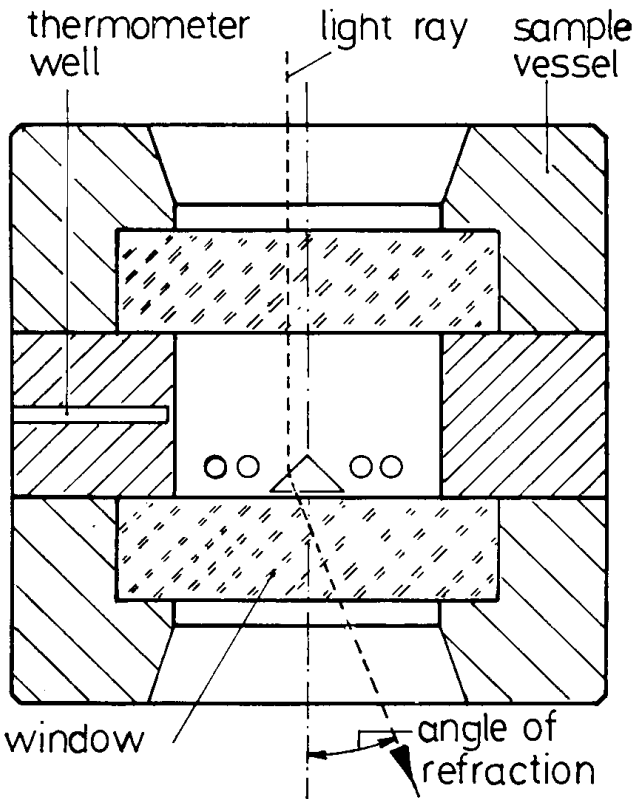
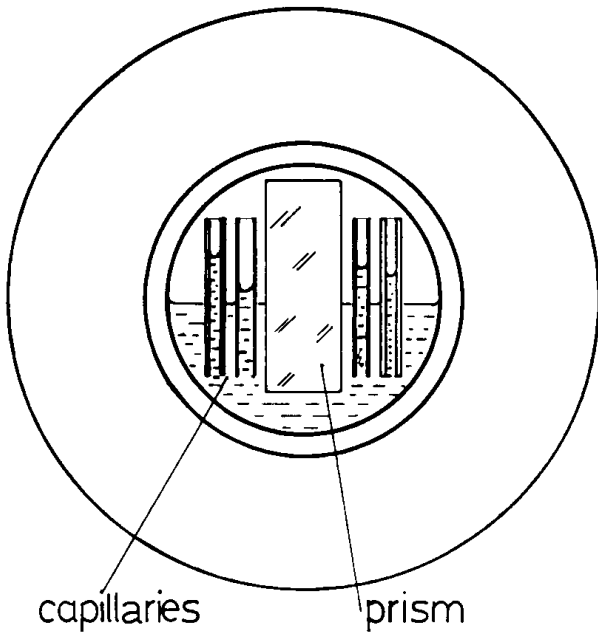


Fig. 1 — Sample vessel.

The critical temperature t_c has been determined visually by observing the reappearance of the meniscus to $t_c = 45.48^\circ\text{C}$. The specific refraction R was evaluated from liquid-vapour density data [11, 12] in the temperature range from 3°C – 40°C . An average value was found, $R = (7.7385 \pm 0.04) \cdot 10^{-2} \text{ cm}^3/\text{g}$. With this value and equation (5) the actual equation of the coexistence curve is obtained

$$(\rho_l - \rho_v) = \rho_c \cdot (3.868 \pm 0.03) (1 - T/T_c)^{0.3422} \text{ g/cm}^3 \quad (7)$$

where the critical density ρ_c is calculated from (6) combined with R to $\rho_c = 0.74 \text{ g/cm}^3$. The actual rectilinear diameter may be represented by

$$(\rho_l + \rho_v)/2 = (1.365 \pm 0.007) - (0.6249 \pm 0.003) \cdot T/T_c \text{ g/cm}^3 \quad (8)$$

Surface tension: Two experimental runs were performed with different charges of SF_6 and with one capillary ($r_4 = 0.32 \text{ mm}$) replaced by a smaller one ($r_5 = 0.051 \text{ mm}$). Since no systematic difference between a_{12}^2 , a_{13}^2 etc. and between run 1 and 2 was observed, average values are used to compute the surface tension from equations (2) and (7). They are listed in table 1.

Table 1
CAPILLARY CONSTANT a^2 AND SURFACE TENSION

Temp. $^\circ\text{C}$	a^2 10^{-3} cm^2	σ dyn/cm	Temp. $^\circ\text{C}$	a^2 10^{-3} cm^2	σ dyn/cm
3.54	5.85	4.099	37.58	1.17	0.463
5.15	5.57	3.852	38.78	1.04	0.389
9.65	4.94	3.283	40.12	0.893	0.310
14.50	4.34	2.745	41.51	0.619	0.194
18.71	3.76	2.259	41.89	0.519	0.173
19.82	3.62	2.148	42.63	0.451	0.126
21.79	3.39	1.956	42.93	0.408	0.109
23.6	3.18	1.785	43.01	0.388	0.103
25.11	2.94	1.610	43.19	0.332	0.0861
26.0	2.79	1.506	43.60	0.284	0.0689
26.74	2.75	1.461	43.87	0.239	0.0549
28.08	2.55	1.323	44.03	0.218	0.0483
29.39	2.37	1.196	44.38	0.166	0.0335
30.2	2.26	1.122	44.42	0.148	0.0294
30.9	2.18	1.064	44.53	0.143	0.0275
31.36	2.11	1.018	44.541	0.132	0.0259
32.21	1.99	0.941	44.543	0.146	0.0280
33.02	1.87	0.863	44.549	0.122	0.0232
33.06	1.85	0.857	44.81	0.0659	0.0117
34.48	1.61	0.716	44.83	0.0652	0.01099
35.26	1.52	0.657	44.967	0.0513	0.00796
35.91	1.46	0.617	45.48	0	0
36.94	1.32	0.537	-20°	—	8.02 (*)
37.1	1.26	0.508	-50°	—	11.63 (*)

(*) From Ref. [13].

For temperatures below $T/T_c = 0.992$ the values of a^2 can be represented, within the experimental error, by

$$a^2 = (3.9408 \pm 0.05) 10^{-2} (1 - T/T_c)^{0.943 \pm 0.004} \text{ cm}^2 \quad (9)$$

Finally combining equations (9) and (7) with (2) one obtains for the surface tension

$$\sigma = (55.31 \pm 0.79)(1 - T/T_c)^{1.2856 \pm 0.004} \text{ dyn/cm} \quad (10)$$

The data points above $T/T_c = 0.992$ ($t = 43^\circ\text{C}$) show greater scatter probably due to increasing experimental uncertainties and are therefore not included in the linear least square fit leading to equation (10).

DISCUSSION OF RESULTS

According to Ferguson and Kennedy [15] the parameter σ_0 of the relation $\sigma = \sigma_0 (1 - T/T_c)^n$ should be related to the critical temperature T_c and critical volume V_c by $\sigma_0 = 3.12 T_c V_c^{-0.55}$, one obtains with $T_c = 318.63 \text{ K}$ and $V_c = 196.9 \text{ cm}^3/\text{moles}$, $\sigma_0 = 54.4 \text{ dyn/cm}$, which is in good agreement with our result $\sigma_0 = 55.3 \text{ dyn/cm}$.

The exponent $n = 1.286$ is higher than that suggested by Ferguson, who gave $n = 1.21$ as the mean of about 40 organic liquids as well as the value $n = 11/9$ proposed by Guggenheim [2], but is in better agreement with $n = 1.28$, which was theoretical obtained by Widom [3] for a three dimensional lattice gas.

The shape of the coexistence curve as characterised by $\rho_l - \rho_v \propto (1 - T/T_c)^\beta$ with $\beta = 0.342$ (equ. (5) and (7)) agrees well with a recently reported value $\beta = 0.348$ [14] and $\beta = 0.344$ obtained by summarizing the density data used to compute the specific refraction.

The average value of the specific refraction $R = 7.7385 \cdot 10^{-2} \text{ cm}^3/\text{g}$ compares well with R of gaseous SF_6 at 0°C and 760 Torr, which was found to be $R = 7.75 \cdot 10^{-2} \text{ cm}^3/\text{g}$ [13]. This should prove that deviations of the Lorentz-Lorenz function are small and that the optical method is suitable to evaluate density data, at least in a limited temperature range.

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DISCUSSION

H. KNAPP (Germany, Fed. Rep.) — There are various methods to measure surface tension. Why did you choose the capillary method for your experiments?

W. RATHJEN — The capillary rise method seems to us the most convenient and accurate method of determining the temperature dependence of surface tension,

particularly in a temperature range up to the critical region, where problems concerning thermodynamical equilibrium become significant. Moreover the comparison with measurement of SF_6 presented by Widom and Webb (U.S.A.) at the "Van der Waals Centennial Conference on Statistical Mechanics" (Amsterdam, August 1973) were obtained by a method using the characteristic of light reflection caused by capillary waves and this shows that the results may be regarded as equivalent.

Our result is: $\sigma = (55,31 \pm 0,79) (1 - T/T_c)^{1,2856}$,

their results are: $\sigma = 55,1 (1 - T/T_c)^{1,285}$.