length of light but smaller ones may occur for the milder treatment used in this study. In the initial stages of oxidation the metal surface is only partly covered with oxide. It is generally considered that the oxidation starts out at a limited number of points and spreads out laterally. It is possible that the oxidation selectively attacks the edges and points of the protuberances in such a manner as to smooth out the surface. A satisfactory analysis of the mechanism by which the surface structure changed during oxidation is beyond the scope of this paper. It seems experimentally true, however, for the surfaces considered that the smaller irregularities were the first to disappear during oxidation. If this be true, the rapid initial decrease of surface during oxidation may suggest that the smallest irregularities contribute the most to the area of the roughened surface. A rough clue as to their dimensions may be had by constructing a hypothetical surface of a suitable distribution of regular pyramidal protuberances. Their size would vary from 5 to 100 Å. for the surface of Fig. 5 and their distribution would be chosen so as to reproduce the observed surface area effect, assuming the effect of oxidation is to smooth out larger and larger protuberances. This particular hypothetical surface would suffer a decrease in surface area of 82% when all the protuberances 35 Å. in height or less disappeared. Since each model surface was unique to the corresponding real surface, it is possible that the value of the average maximum protuberance size calculated for the artificial surface had some real significance for the actual surface at least as an order of magnitude. The analysis is a very simple illustration of a possible technique for systematically defining relative surface irregularities on a molecular scale using controlled oxidation data together with surface area data.

Acknowledgments.—The writer is indebted to C. S. Smith, C. S. Barrett and E. A. Gulbransen for discussions and also to J. Cerny, W. Bergmann and J. Hess for the preparation of samples. The microbalance was built by W. Mankowich, J. Getzholz and T. O'Donnell and their craftsmanship is also acknowledged. The research was done under U. S. Army Air Force Contract AF-33 (038)-6534.

Conclusions

1. The true surface areas of metal surfaces as small as 10 cm.^{2} have been measured with an error of 6% from low temperature adsorption isotherms using a specially designed vacuum microbalance technique. This method is of special value in determining the average thickness of corrosion films formed by the reactions of gases or liquids with solids.

2. The isosteric heats of adsorption corresponding to an adsorption of one monolayer of nitrogen are found to be 3500 cal./mole on the (100) face of copper and 2500 cal./mole on the polycrystal face for the particular surfaces studied.

3. The effect of the progressive oxidation of a rough polycrystalline surface of copper was to decrease the surface area to a point where the roughness factor approached unity. The analogous effect on a very simple hypothetical surface was considered.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

Solubility of Perfluoro-*n*-heptane with Benzene, Carbon Tetrachloride, Chloroform, *n*-Heptane and 2,2,4-Trimethylpentane

BY J. H. HILDEBRAND, B. B. FISHER AND H. A. BENESI

The work reported in this paper is a further contribution to the general investigation of the solubility relations of fluorocarbons that has been going on in this laboratory for several years,[1] and is a sequel, in particular, to the similar determinations with perfluoromethylcyclohexane.[1f] The extremely low internal pressures of the fluorocarbons makes it possible to study miscibilities of these liquids with other non-polar liquids in a convenient temperature range. Since perfluoro-*n*-heptane has even a lower internal pressure than perfluoromethylcyclohexane it was to be expected that perfluoroheptane would show slightly higher critical mixing temperatures with any other liquid.

Experimental Section.—Spectrophotometric measurements revealed that commercial perfluoro-*n*-heptane (C_7F_{16}) strongly absorbed at 210 mμ, this absorption presumably arising from unsaturated impurities. After passing the fluoroheptane through a 2 meter long, 1 cm. diameter, silica gel column, the absorption at 210 mμ was negligible. The product was then distilled twice through a 30-plate fractionating column at a 30:1 reflux ratio, the course of the fractionation being followed by density measurements at 25°. The densities of the fractions making up the final product ranged from 1.72062 to 1.72101 g./ml. at 25°. A mass spectrometric analysis of this product, kindly made by the Shell Development Company at Emeryville, California, revealed the presence of impurities to which were assigned the empirical formulas, C_7F_{14}, $C_7F_{15}H$, and $C_7F_{14}H_2$. Since these impurities did not total

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[1] (a) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **70**, 3978 (1948); (b) R. L. Scott, *ibid.*, **70**, 4090 (1948); (c) J. C. Gjaldbaek and J. H. Hildebrand, *ibid.*, **71**, 3147 (1949); (d) J. H. Hildebrand, *J. Phys. Coll. Chem.*, **53**, 944 (1949); (e) J. H. Hildebrand, H. A. Benesi and L. M. Mower, THIS JOURNAL, **72**, 670 (1950); (f) J. H. Hildebrand and D. R. F. Cochran, *ibid.*, **71**, 22 (1949).

TABLE I

CONSOLUTE TEMPERATURES OF SOLUTIONS OF PERFLUORO-*n*-HEPTANE AT VARIOUS VOLUME FRACTIONS AND MOLE FRACTIONS OF THE OTHER COMPONENT

C_6H_6	ϕ_2	0.100	0.193	0.300	0.425	0.501	0.618	0.655	0.707	0.800	0.900
	x_2	0.220	0.374	0.518	0.650	0.717	0.802	0.827	0.859	0.910	0.958
	t	56.6	85.8	102.1	109.9	113.1	113.4	113.3	112.5	107.6	92.2
$CHCl_3$	ϕ_2	0.089	0.197	0.300	0.407	0.505	0.611	0.704	0.796	0.905	
	x_2	0.224	0.405	0.545	0.642	0.740	0.814	0.872	0.915	0.964	
	t	24.6	55.8	69.9	75.7	78.2	78.4	77.3	72.8	55.8	
CCl_4	ϕ_2	0.097	0.187	0.300	0.396	0.495	0.603	0.708	0.800	0.900	
	x_2	0.199	0.348	0.499	0.604	0.687	0.779	0.850	0.903	0.954	
	t	2.8	32.3	49.1	55.9	58.4	58.7	57.6	53.3	33.4	
n-C_7H_{16}	ϕ_2	0.151	0.211	0.303	0.366	0.400	0.505	0.609	0.706	0.809	0.907
	x_2	0.214	0.291	0.400	0.469	0.504	0.609	0.707	0.787	0.865	0.938
	t	27.3	36.5	45.8	48.5	49.3	50.0	49.9	48.5	42.1	24.0
2,2,4-$(CH_3)_3$-C_5H_9	ϕ_2	0.205	0.315	0.398	0.516	0.614	0.715	0.810			
	x_2	0.255	0.377	0.467	0.584	0.677	0.768	0.845			
	t	10.6	19.8	22.8	23.7	23.6	22.2	16.9			

TABLE II

VOLUME FRACTIONS AND SOLUBILITY PARAMETERS AT CRITICAL SOLUTION TEMPERATURES

Solvent	t_c,°C.	$\phi_{2,c}$ vol. fr.	v_2 ml. per mole	v_1	δ_2 (cal./ml.)$^{1/2}$	δ_1	$\delta_2 - \delta_1$ obs.	Eq. 5	Eq. 7
i-C_8H_{18}	23.7	0.550	165.8	225	6.88	5.87	1.01	2.47	2.48
n-C_7H_{16}	50.0	.540	152.3	235	7.13	5.55	1.58	2.58	2.61
CCl_4	58.7	.578	101.3	239	8.13	5.45	2.68	2.78	2.97
$CHCl_3$	78.5	.578	86.9	248	8.42	5.20	3.22	2.90	3.19
C_6H_6	113.5	.594	100.7	268	7.84	4.73	3.11	2.89	3.15

more than 1–2% and probably had solvent powers not very different from that of perfluoro-*n*-heptane, we used this product without further treatment.

Commercial carbon tetrachloride was fractionally distilled through a 30-plate column at a reflux ratio of 30:1. The densities of the fractions that were later combined and used in this investigation ranged from 1.58438 to 1.58440 g./ml. at 25°. This can be compared to the I.C.T. value, 1.58434 g./ml. at 25°.[2] Commercial chloroform was similarly purified. The final product had a density of 1.47928 g./ml. at 25°, compared with the I.C.T. value, 1.47955.[2]

Pure grade *n*-heptane by Philips Petroleum Company was given the silica gel treatment described above to remove unsaturated impurities. The product was then dried over "Drierite" and distilled. The density of the *n*-heptane before purification was 0.67563 g./ml. at 25°; after purification, 0.67954 g./ml. This value compares favorably with 0.67947 g./ml. at 25° by the Bureau of Standards.[3] Isoöctane (2,2,4-trimethylpentane) by Shell Development Company was similarly purified. The density of the product was 0.68785 g./ml. at 25°, compared with 0.68781 by the Bureau of Standards.[3] The benzene was that used by Benesi and Hildebrand.[4]

The apparatus and procedure were essentially the same as in the previous investigation.[1f]

Data and Discussion.—The observed consolute temperatures are given in Table I for solutions of different contents of the other component expressed both as volume fraction, φ_2, and mole fraction, x_2. The volume fractions are for 25°, but are practically unaffected by temperature within the ranges here used. To show the effect of composition units on the symmetry of the curves, the points are plotted against x_2 in Fig. 1, and in Fig. 2 against φ_2. The maxima of these curves are taken as the critical solution temperatures and are given in Table II, together with the critical compositions. The column headings in Table II bearing the subscript 1, refer to the fluoroheptane; the subscript 2, refers to the other components.

We shall discuss these data in terms of the two now well known equations[5]

$$\ln (a_2/x_2) = v_2\phi_1^2 (\delta_1 - \delta_2)^2/RT \qquad (1)$$

$$\ln(a_2/\phi_2) = v_2\phi_1^2 (\delta_1 - \delta_2)^2/RT + \phi_1(1 - v_2/v_1) \qquad (2)$$

where a_2 is the activity and x_2 is the mole fraction of component 2, the ϕ's are volume fractions, and the v's are the molar volumes and the δ's (solubility parameters) the square root of the energies of vaporization per ml. of the pure components. The former is the equation for "regular" solutions, applicable to components whose molar volumes are not significantly different; the latter takes account of such inequality. Solvation and association are assumed absent in both cases. At the critical point, d ln $a_2/\mathrm{d}x_2 = 0$ and $\mathrm{d}^2 \ln a_2/\mathrm{d}x_2^2 = 0$. Applying these conditions to Eq. 1 gives, as has long been known[6]

$$x_{2,c} = \frac{(v_1^2 + v_2^2 - v_1v_2)^{1/2} - v_2}{v_1 - v_2} \qquad (3)$$

and

$$RT_c = \frac{2x_1x_2v_1^2v_2^2}{(x_1v_1 + x_2v_2} (\delta_2 - \delta_1)^2 \qquad (4)$$

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[2] "International Critical Tables," Vol. III, p. 28.

[3] "Selected Values of Properties of Hydrocarbons," Bureau of Standards Circular C461, Government Printing Office, Washington, D. C., 1947.

[4] H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949).

[5] *Cf.* J. H. Hildebrand, *Chem. Rev.*, **44**, 37 (1949); also ref. 1.

[6] J. H. Hildebrand and R. L. Scott, "Solubility of Non-Electrolytes," 3rd edition, Reinhold Publ. Corp., New York, N. Y., 1950.

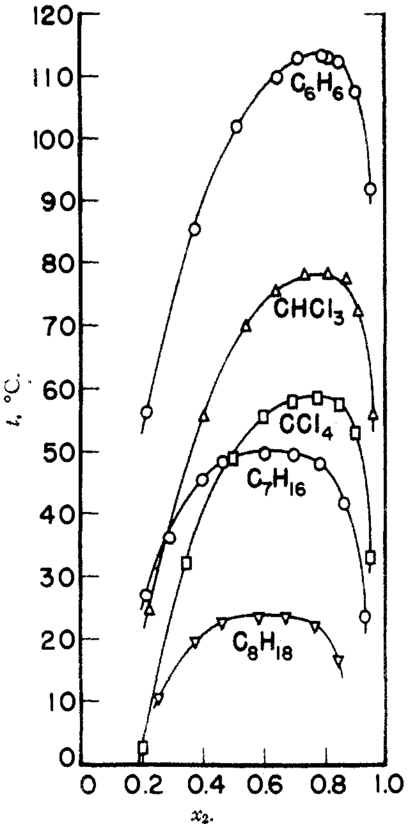

Fig. 1.—Mole fraction of second component.

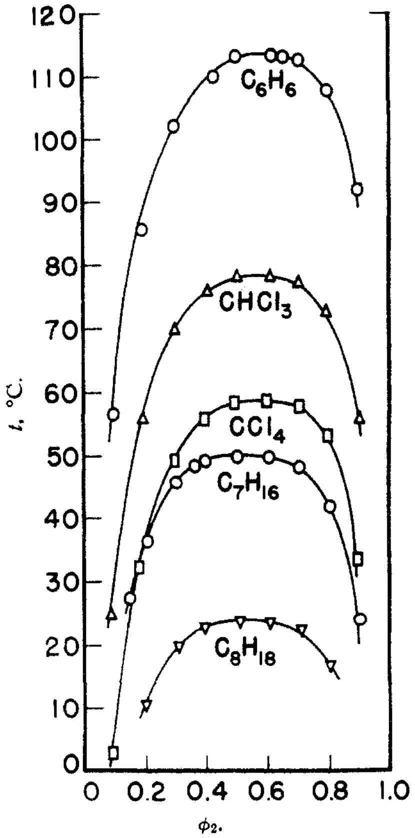

Fig. 2.—Volume fraction of second component.

To eliminate x_1 and x_2 from Eq. 4 by substituting Eq. 3, and its conjugate, gives a complicated equation; therefore, it is preferable to obtain the numerical values of x_1 and x_2 by aid of Eq. 3 and substitute these in Eq. 4. A simpler, approximate equation can be derived from Eq. 4 by utilizing the fact that the critical composition is in general close to $\phi_1 = \phi_2 = 0.5$. Eq. 4 can be rewritten

$$RT_c = \frac{2\phi_1\phi_2\, v_1v_2\, (\delta_2 - \delta_2)^2}{x_1v_1 + x_2v_2} \qquad (4')$$

If we apply the above condition, we obtain $x_1v_1 = x_2v_2$ from which it follows that $x_1 = v_2/(v_1 + v_2)$ and $x_2 = v_1/(v_1 + v_2)$. Substituting the latter expressions for x_1 and x_2 in Eq. 4,[1] we then obtain[7]

$$RT_c = 0.25\ (v_1 + v_2)\ (\delta_2 - \delta_1)^2 \qquad (5)$$

But in dealing with fluorocarbons, whose molal volumes are large compared with such substances as chloroform and benzene, it is desirable to obtain expressions for the critical composition and temperature from Eq. 2. In this case we can take the first and second derivatives of ln a_2 with respect to ϕ_2, set both equal to zero and solve, and obtain

$$\varphi_{2,c} = v_1^{1/2}/(v_1^{1/2} + v_2^{1/2}) \qquad (6)$$

and

$$RT_c = \frac{2v_1v_2}{(v_1^{1/2} + v_2^{1/2})^2}\,(\delta_2 - \delta_1)^2 \qquad (7)$$

Let us first compare Eqs. 3 and 6 with experiment, using C_7F_{16} and CCl_4, with v_1 = 239 and v_2 = 101 at t_c = 58.7°. Eq. 3 gives x_2 = 0.775 from which $\phi_{2,c}$ = 0.59; Eq. 6 gives $\phi_{2,c}$ = 0.61, while the diameter of the curve in Fig. 2 gives 0.58. The differences are not significant.

Next, let us compare Eqs. 5 and 7 by substituting the experimental values of T_c and the molal volumes at these temperatures in those equations and calculating $\delta_2 - \delta_1$, and comparing the results with the differences between the solubility parameters for the individual liquids, allowing for the effect of temperature. The variation of the heat of vaporization with temperature is seldom known with accuracy; therefore, in order to treat all the liquids here involved by a uniform method, we have used a reasonably valid formula connecting δ with the molar volume[6]

$$\frac{d \ln \delta}{d \ln v} = -1.25 \qquad (8)$$

In those cases where the critical temperatures were close to the boiling points of any of the liquids, the values of δ predicted by means of this relation agreed well with values calculated from direct calorimetric determinations at the boiling point. The observed values of $\delta_2 - \delta_1$, so cal-

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(7) The approximation involved in obtaining Eq. 5 from Eqs. 3 and 4 is very good, because if we take v_1 = 200 and v_2 = 100, the volume function in Eq. 4 takes the value 76.8, while in Eq. 5 it is 75, an agreement well within the general limits of accuracy of the theory. Consequently, for systems such as the ones here considered, the simplicity of Eq. 5 makes it more useful than Eq. 3.

culated, are compared with the values predicted by Eqs. 5 and 7 in the last three columns of Table II.

We see that Eqs. 5 and 7 agree more closely the nearer v_2/v_1 is to unity. In the cases with isoöctane and with heptane, the two values are practically identical but they differ by 0.3 with chloroform, where the volume discrepancy is largest.

There is a very large discrepancy, however, between both of these equations and experiment for solutions of perfluoroheptane with isoöctane and with normal heptane, which behave as if the δ-values of these substances were much higher than the values derived from heats of vaporization. The same can be inferred from the data for iodine solutions,[1e] which give δ_2-values for iodine considerably less in its solutions with isoöctane, *n*-hexane and *n*-heptane than in the other solvents. These paraffins are poorer solvents for fluorocarbons and better solvents for iodine and phosphorus[8] than would be concluded from their heats of vaporization. For practical purposes, one might adjust their values empirically, but curiosity is naturally aroused about the reasons for discrepancies of this magnitude. We are at present engaged in measuring volume changes of mixing of appropriate binary systems to see if these inconsistencies can be attributed to changes of packing during the mixing process. We expect to publish our findings together with a more detailed analysis of liquid–liquid solubilities in a forthcoming publication.

We gratefully acknowledge support of the Atomic Energy Commission for this research.

Summary

Liquid–liquid solubility curves have been determined for binary mixtures of perfluoro-*n*-heptane with benzene, carbon tetrachloride, chloroform, *n*-heptane and 2,2,4-trimethylpentane. The critical temperatures obtained from these curves were 113.5°, 58.7°, 78.5°, 50.0° and 23.7°, respectively.

Solubility parameter differences calculated from experimental results were in close agreement with values predicted by solubility theory for all but the two paraffin hydrocarbons listed above.

BERKELEY, CALIF. RECEIVED APRIL 11, 1950

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[CONTRIBUTION FROM THE INSTITUTE FOR THE STUDY OF METALS, UNIVERSITY OF CHICAGO]

Preparation of Single Crystals of Manganous Fluoride. The Crystal Structure from X-Ray Diffraction. The Melting Point and Density

BY MAURICE GRIFFEL[1] AND J. W. STOUT

In connection with the determination of the magnetic anisotropy of MnF_2 reported elsewhere[2] single crystals were grown from the melt. The method of growing the crystals will be briefly described here, together with measurements that were made of the melting point, the density and the crystal parameters as determined from X-ray diffraction.

Preparation of Single Crystals.—Powdered MnF_2 was prepared by the method of Kurtenacker, Finger and Hey.[3] $MnCO_3$ was precipitated from a solution of analytical reagent $MnSO_4 \cdot H_2O$. In order to avoid precipitation of $MgCO_3$ an excess of the $MnSO_4$ solution was used. The $MnCO_3$ was converted to MnF_2 by adding it to a 20% aqueous HF solution contained in a plastic dish. The precipitated MnF_2 was washed several times with water and a water–ethanol mixture and then dried under vacuum. When the MnF_2 so prepared was melted under a vacuum of about 10^{-4} mm. the resulting product was greenish. The original powder could be dried for a day at 300° under a vacuum of 10^{-5} mm. with no change in appearance, but further heating under vacuum to 600 to 800° would cause a darkening of the light pink color. The darkening and development of green color were presumably due to the reaction of the MnF_2 with traces of water that were not completely removed by the drying procedure. To avoid this the drying of the powder and the growing of the crystals from the melt were carried out in a stream of anhydrous HF. Under these conditions no discoloration was observed.

The apparatus for growing the crystals was similar to that described by Stockbarger.[4] Because of the necessity of maintaining an atmosphere of HF the central tube was made of nickel pipe, 6.67 cm. o. d. and 6.27 cm. i. d. The crucible was supported inside this tube on top of a capped nickel pipe, 1.11 cm. o. d., which could be raised and lowered at different rates by an electric motor and a train of gears. The outer nickel pipe was provided with entrance and exit tubes for the HF gas and the seals at the top and bottom were made with polytetrafluorethylene ("teflon") gaskets. Because of corrosion by the HF the nickel pipe had to be replaced after about 500 hours operation at 950°. The outer nickel pipe was surrounded by a heating unit of nichrome wire wound on an alundum form. Chromel–alumel thermocouples were used for temperature measurements and the temperature was controlled by a thermocouple and a proportioning temperature regulator.[5] The crucibles used were made of high purity graphite. Preliminary experiments showed that, after melting, the MnF_2 adhered tightly to platinum but could be easily removed from graphite. A typical crucible was of cylindrical form, 1.91 cm. o. d., wall thickness 0.17 cm. and depth 6 cm. The inner diameter was slightly tapered toward the bottom and ended in a cone of thirty degree half-angle.

Finely divided MnF_2, precipitated and dried at room temperature, was placed in a platinum boat in a furnace

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[1] Atomic Energy Commission Fellow 1948–1949. Present address: Iowa State College, Ames, Iowa.

[2] J. W. Stout and Maurice Griffel, *Phys. Rev.*, **76**, 144 (1949). A more detailed account will be published in the *Journal of Chemical Physics*.

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