solution (0.0144 g. Mn/ml.) and weights of manganese carbonyl were sealed in glass ampoules under nitrogen:

Sample	1	2	3	4
Vol. ketyl soln. (ml.)	9.85	8.0	9.90	7.56
Wt. $Mn_2(CO)_{10}$ (g.)	0.4212	0.2443	0.2358	0.1469
Molar ratio (ketyl:carbonyl)	2.38	3.34	4.29	5.27
Color after 2 days	Orange	Orange	Orange-red	Red

After standing for two days at room temperature, the tubes were opened and the infrared spectra of the solutions were obtained. The 5.0 μ (manganese carbonyl) band was strongest in sample 1 and much weaker in the other three samples. Although the data are not subject to quantitative interpretation, it appears that somewhat in excess of 2.38 moles of manganese benzophenone ketyl will react with one mole of manganese carbonyl.

In order to study the products of the ketyl–carbonyl reaction, two hydrolysis experiments were carried out. In the first experiment, a 20-ml. sample of the THF–ketyl solution was poured into 100 ml. of 10% acetic acid. The solution was extracted with ether, and the extract was washed with 5% potassium bicarbonate solution and with water. The ether was distilled, and the residue was analyzed by infrared spectroscopy. In the second experiment, 2.5 g. of manganese carbonyl was dissolved in 20 ml. of THF–ketyl solution, and the mixture was let stand for 30 minutes. The molar ratio of carbonyl to ketyl was 1.22. The solution was hydrolyzed, worked up and analyzed in the same manner as the control experiment with ketyl alone. The hydrolysis product from the control experiment contained 15% benzophenone and 79% benzpinacol, while the hydrolysis product from the reaction of manganese carbonyl with the ketyl solution contained 24% benzophenone, 23% benzpinacol and about 50% manganese carbonyl. These data show that benzophenone is produced by the reaction of the ketyl with manganese carbonyl.

DETROIT 20, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF FLORIDA]

Free Energy Relations in Fluorocarbon–Hydrocarbon Systems

BY B. G. KYLE[1] AND T. M. REED, III

RECEIVED JUNE 25, 1958

The mutual solubility curves have been determined for 14 fluorocarbon–hydrocarbon systems. The equations of Hildebrand fail to predict consolute temperatures of these systems although consolute compositions are satisfactorily predicted. Examples are given which show that the agreement between observed and calculated consolute temperature is not a good criterion for testing the applicability of the Scatchard–Hildebrand theory. The total vapor pressures of some fluorocarbon–hydrocarbon mixtures were measured in the two liquid phase region. It is shown that excess free energies of mixing in binary fluorocarbon–hydrocarbon systems can be estimated quite well from mutual solubility data through the use of Van Laar equations. An empirical correlation is also presented for the estimation of excess free energies of mixing or consolute temperatures in fluorocarbon–paraffin hydrocarbon systems from properties of the pure components. This correlation is based on a negative excess entropy of mixing at constant volume.

Experimental

Materials.—Most of the hydrocarbons used in this work were obtainable commercially in a reasonable degree of purity and were not further purified. The physical properties of these compounds are listed in Table I along with the reported literature values.

TABLE I

PHYSICAL PROPERTIES OF MATERIALS

Compound	Refractive index 25° Expt.	Refractive index 25° Lit.	Density 25° (g./ml.) Expt.	Density 25° (g./ml.) Lit.	B.p. 1 atm. (°C.) Expt.	B.p. 1 atm. (°C.) Lit.
n-Heptane	1.3852	1.38511[2]	0.6798	0.67951[2]	98.4	98.427[2]
Methylcyclohexane	1.4206	1.42058[2]	.76511	.76506[2]	100.9	100.934[2]
Toluene	....	.....	.86232	.86230[2]	110.7	110.625[2]
Carbon tetrachloride	1.4567	1.4573[3]	1.5844	1.5845[3]	...	.....
2-Butanone	1.3761	1.37643[2]	0.7995	0.79970[2]	79.6	79.59[2]
Perfluoroheptane (C_7F_{16})	1.2594	1.25818[4]	1.7258	1.71802[4]	82.1	82.5[4]
Perfluorocyclic oxide ($C_8F_{16}O$)	1.2770	.....	1.7633	......	102.8	.....
1-Hydroperfluoroheptane ($C_7F_{15}H$)	1.2700	1.2718[5]	1.7233	......	95.4	94–95[5]
Perfluorotributylamine [$(C_4F_9)_3N$]	1.2906	.....	1.8772	......	177.6	.....
Methyl perfluoroöctanoate [$C_7F_{15}COOCH_3$]	1.3033	.....	1.6967	......	160.8	.....

Five fluorocarbon compounds were used in this work. The physical properties of these compounds are also listed in Table I. The physical properties of some of these fluorocarbons have been reported in the literature; these values are also included in Table I.

Perfluorocyclic Oxide ($C_8F_{16}O$).—This material was the major constituent in "Fluorochemical O-75" manufactured by the Minnesota Mining and Manufacturing Company. It is believed that this fluorocarbon is a five- or six-membered oxygen-containing ring with side chains. This material first was fractionated in a laboratory distillation column. The center cut from this fractionation was further purified by an azeotropic distillation with *n*-heptane.

The fluorocarbon then was separated from the *n*-heptane by cooling the azeotrope to Dry Ice Temperature where the liquid phases were found to have very low mutual solubility. The perfluorocyclic oxide now was freed from the small amount of remaining *n*-heptane by redistillation. This purified material exhibited only one peak when subjected to chromatographic analysis using a partitioning liquid found to be especially good at resolving fluorocarbon mixtures.[6]

---

[1] Department of Chemical Engineering, Kansas State College, Manhattan, Kansas.

[2] American Petroleum Institute Research Project 44, "Selected Values of Properties of Hydrocarbons," National Bureau of Standards, Washington, D. C., 1950.

[3] J. Timmermans, "Physio-Chemical Constants of Pure Organic Compounds," Elsevier Publ. Co., New York, N. Y.

[4] G. D. Oliver, S. Blumkin and C. W. Cunningham, THIS JOURNAL, **73**, 5722 (1951).

[5] E. P. McLaughlin and R. L. Scott, *J. Phys. Chem.*, **60**, 674 (1956).

[6] T. M. Reed, III, *Anal. Chem.*, **30**, 221 (1958).

Perfluoroheptane (C_7F_{16}).—This material was a constituent of "Fluorochemical 101" marketed by The Minnesota Mining and Manufacturing Company and was purified by the same procedure as perfluorocyclic oxide. A chromatographic analysis of this material revealed only one peak.

Perfluorotributylamine [$(C_4F_9)_3N$].—This material was the center cut obtained by fractionation of Minnesota Mining and Manufacturing Company's "Fluorochemical N-43." Chromatographic analysis revealed that this material was a mixture of several components, probably isomers.

1-Hydroperfluoroheptane ($C_7F_{15}H$).—This material was prepared by Dr. H. C. Brown in these laboratories by the dicarboxylation of the sodium salt of perfluoroöctanoic acid. This material was purified by fractional distillation.

Methyl Perfluoroöctanoate ($C_7H_{15}COOCH_3$).—This compound was prepared by Dr. H. C. Brown from perfluorooctanoic acid and was purified by fractional distillation.

Solubility.—The solubility apparatus consisted of a heavy-walled glass test-tube clamped between two stainless steel flanges by means of four bolts. A Teflon gasket placed between the open end of the tube and the top flange was used to seal the tube. A thermocouple, which passed through the top flange, was used to measure the temperature of the mixture. The whole tube assembly was immersed in an oil- or water-bath, which provided the necessary temperature control.

The unmixing temperature of a known binary mixture was determined by heating the mixture until the two liquids were completely miscible, then cooling the solution slowly while shaking and observing the temperature at which the second liquid phase appeared. The solubility curves on Fig. 1–5 were obtained by plotting the unmixing temperature–composition data. For comparison the data of Hildebrand, Fisher and Benesi[7] for the two perfluoroheptane systems are also plotted on Fig. 1. The small differences between the present data and that of Hildebrand, *et al.*, could be due to the difficulty in accurately determining unmixing temperatures caused by opalescence or due to the differences in composition of the perfluoroheptane used.

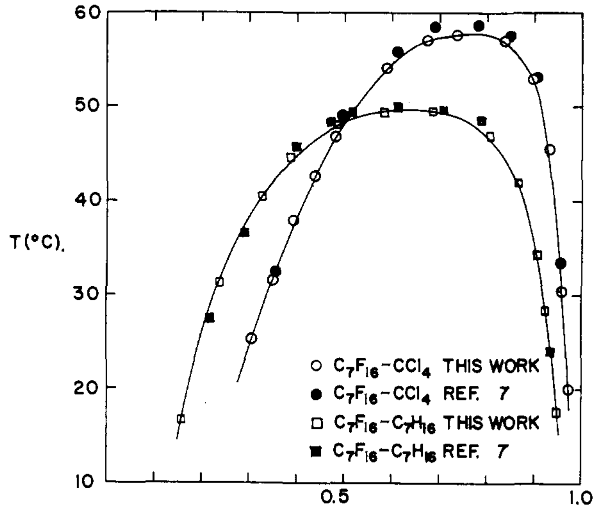

Fig. 1.—Binary solubility curves, systems containing C_7F_{16}.

Total Vapor Pressure.—A dynamic still, shown on Fig. 6, was used for these measurements. The still was designed so that vigorous boiling and low liquid level would prevent superheating while the insulating vapor space would prevent any appreciable heat loss by the vapor in the inside tube. During operation of the still under equilibrium conditions, no condensation was observed inside the inner tube. A calibrated thermocouple was used to measure the vapor temperature. The still was connected to a vacuum system containing a mercury manometer which could be read to the nearest tenth of a millimeter by use of a cathetometer.

As a check on the performance of the still, the total pressure of the system 2-butanone–water was determined at two temperatures. These values compare favorably with the reported literature values[8] as shown in Table II.

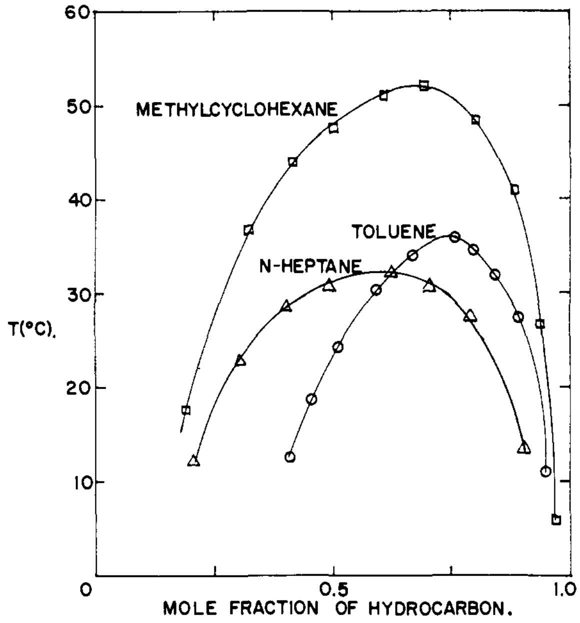

Fig. 2.—Binary solubility curves, systems containing $C_7F_{15}H$.

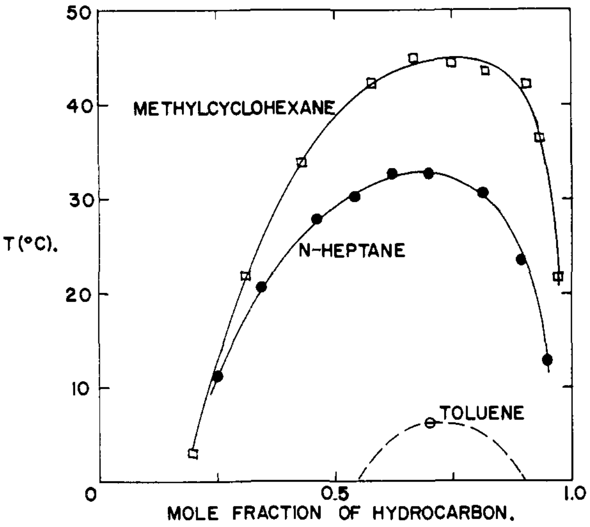

Fig. 3.—Binary solubility curves, systems containing $C_7F_{15}COOCH_3$.

TABLE II

CHECK RUN IN TWO-LIQUID PHASE STILL SYSTEM: 2-BUTANONE–WATER[8]

Ref. 8		This work	
Pressure, mm.	Temp., °C.	Pressure, mm.	Temp. °C.
760	73.3	768	73.6
500	62.0	503	62.0

Consolute Temperatures

The consolute temperatures and compositions of twelve systems reported in this work are listed in Table III along with the consolute temperature and

---

(7) J. H. Hildebrand, B. B. Fisher and H. A. Benesi, THIS JOURNAL, 2, 4348 (1950).

(8) D. F. Othmer and R. F. Benenati, *Ind. Eng. Chem.*, 37, 299 (1945).

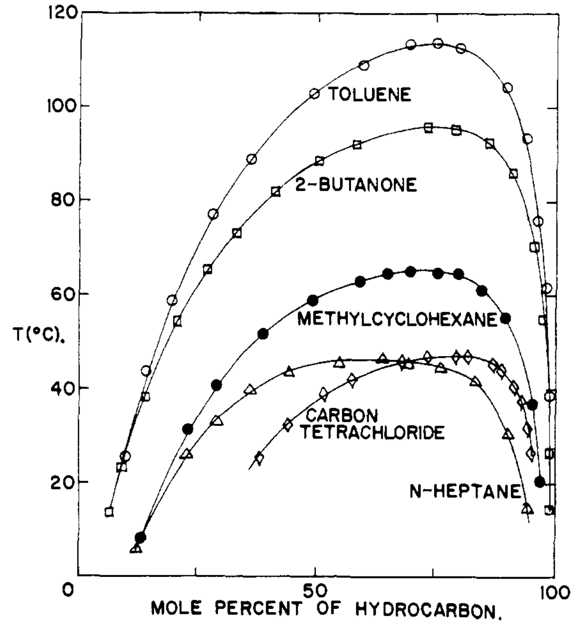

Fig. 4.–Binary solubility curves, systems containing $C_8F_{16}O$.

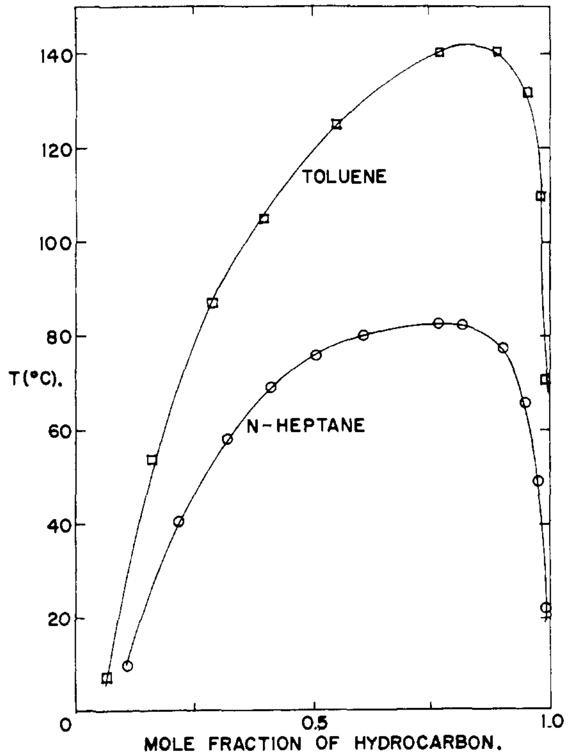

Fig. 5.–Binary solubility curves, systems containing $(C_4F_9)_3N$.

composition as calculated from the equations of Hildebrand[9]

$$RT_c = \frac{2x_1x_2V_1{}^2V_9{}^2(\delta_1 - \delta_2)^2}{(x_1V_1 + x_2V_2)^3} \qquad (1)$$

$$x_1 = \frac{(V_1{}^2 + V_2{}^2 - V_1V_2)^{1/2} - V_1}{V_2 - V_1} \qquad (2)$$

where V is the molal volume, x is the mole fraction and δ is the solubility parameter defined as $\sqrt{\Delta E^v/V}$ where ΔE^v is the energy of vaporization. Subscript one (1) refers to the hydrocarbon.

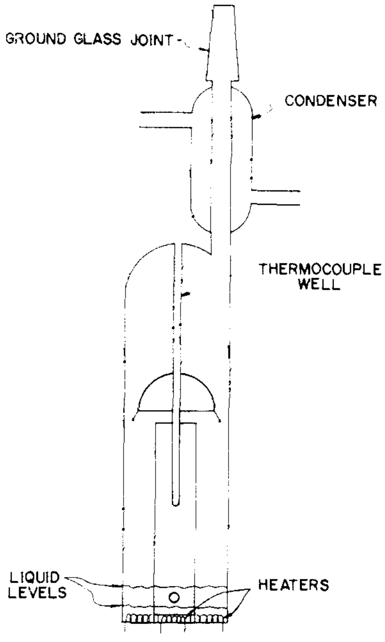

Fig. 6.—Two liquid phase still.

Table III

The Comparison of Calculated and Observed Consolute Temperatures and Compositions

System	Temp., °K. Obsd.	Temp., °K. Eq. 1	Composition Obsd.	Composition Eq. 2
$C_6H_5CH_3$–$C_8F_{16}O$	386	377	0.73	0.77
$C_6H_5CH_3$–$(C_4F_9)_3N$	415	660	.82	.87
$C_6H_5CH_3$–$C_7F_{15}H$	309	266	.75	.74
n-C_7H_{16}–$C_8F_{16}O$	320	130	.63	.67
n-C_7H_{16}–$C_7F_{15}COOCH_3$	306	84	.67	.69
n-C_7H_{16}–$C_7F_{15}H$	305	99	.61	.63
n-C_7H_{16}–$(C_4F_9)_3N$	355	286	.79	.78
$C_6H_{11}CH_3$–$C_8F_{16}O$	338	189	.74	.71
$C_6H_{11}CH_3$–$C_7F_{15}COOCH_3$	318	124	.75	.73
$C_6H_{11}CH_3$–$C_7F_{15}H$	325	140	.69	.68
CCl_4–$C_8F_{16}O$	321	292	.80	.78
$CH_3COC_2H_5$–$C_8F_{16}O$	369	500	.75	.81

The results shown in Table III follow the trend observed with many other fluorocarbon–hydrocarbon systems. Equation 2 predicts reasonable values of the consolute composition while equation 1 in most cases predicts values of the consolute temperature which are far too low. Only for the system perfluorocyclic oxide–toluene does equation 1 predict the correct value of the consolute temperature.

It should be mentioned that although used often in the literature, the comparison of the calculated and observed consolute temperatures is not a good criterion for testing the applicability of the Scatchard–Hildebrand theory. If equations 1 and 2 predict the correct temperature and composition, this means that the first and second derivatives of the activity coefficient with respect to composition are equal to the corresponding derivatives of the activity coefficient as given by the Scatchard–Hildebrand theory. This is a necessary, but not a suf-

---

[9] J. H. Hildebrand and R. L. Scott, "Solubility of Nonelectrolytes," 3rd Ed., Reinhold Publ. Co., New York, N. Y., 1950.

ficient condition which must be met by the Scatchard–Hildebrand equation for activity coefficients, for it is conceivable that two different functions could have equal first and second derivatives at a given composition. This reasoning can be substantiated by comparing activity coefficients determined from binary solubility data with those calculated from the Scatchard–Hildebrand equations

$$RT \ln \gamma_1 = V_1(\delta_1 - \delta_2)^2\phi_2^2 \qquad (3)$$

$$RT \ln \gamma_2 = V_2(\delta_1 - \delta_2)^2\phi_1^2 \qquad (4)$$

The term ϕ represents the volume fraction.

Activity coefficients in two liquid phase systems can be calculated from equations 5 and 6 which state the conditions for equilibrium

$$x_1\gamma_1 = x_1'\gamma_1' \qquad (5)$$

$$x_2\gamma_2 = x_2'\gamma_2' \qquad (6)$$

The primed quantities in equations 5 and 6 refer to the hydrocarbon-rich phase and the unprimed quantities refer to the fluorocarbon-rich phase.

In many fluorocarbon–hydrocarbon systems forming two liquid phases, the mole fraction of hydrocarbon in the hydrocarbon-rich phase (x_1') approaches unity at low temperatures thus causing γ_1' to approach unity. By setting γ_1' equal to unity, equation 5 can be used with the solubility data to calculate the activity coefficient of the hydrocarbon in the fluorocarbon-rich phase (γ_1). The natural logarithm of γ_1 so calculated is compared in Table IV with values of ln γ_1 predicted by equation 3 for three systems in which the observed and calculated consolute temperatures are in good agreement.

TABLE IV

TEST OF THE CONSOLUTE TEMPERATURE CRITERION

System[a]	Tc (°K.) Obsd.	Tc (°K.) Eq. 1	Solubility data t (°C.)	Solubility data x_1	Solubility data x_1'	ln γ_1 Eq. 5	ln γ_1 Eq. 3	Ref.
I	323.5	325	26.3	0.306	0.960	1.14	0.913	10
II	358.5	360	61.1	.320	.956	1.09	.900	10
III	386	377	69.0	.256	.981	1.34	.977	This work

[a] I, perfluoromethylcyclohexane–chloroform; II, perfluoromethylcyclohexane–benzene; III, perfluorocyclic oxide–toluene.

One would expect the same percentage difference between the logarithm of the activity coefficients as between the two consolute temperatures in Table IV since both T_c and ln γ_1 are directly proportional to the $(\delta_1 - \delta_2)^2$ term. Inspection of Table IV reveals that the percentage difference between the logarithms of the activity coefficients is much greater than between the consolute temperatures. If the assumption that $\gamma_1' = 1$ were inaccurate, it would cause values of γ_1 as calculated from equation 5 to be lower than their actual values since these systems exhibit positive deviations from Raoult's law ($\gamma_1' > 1$). The actual values of γ_1 would then be higher than calculated from equation 5 which would cause even larger disagreement between the values of ln γ_1 compared in Table IV.

Since the values of T_c and ln γ_1 are compared at different temperatures, the possibility arises that the system conforms to the theory in the range of the consolute temperature, but not at other temperatures. However, from consideration of consolute temperature alone, one would erroneously assume that the three systems listed in Table IV closely conformed to the theory.

Excess Free Energy of Mixing

The Scatchard–Hildebrand equations for the activity coefficients are similar in form to the Van Laar equations which are widely used in correlating and smoothing vapor–liquid equilibrium data. The Van Laar equations are

$$\ln \gamma_1 = A \Big/ \left[\frac{Ax_1}{Bx_2} + 1\right]^2 \qquad (7)$$

$$\ln \gamma_2 = B \Big/ \left[\frac{Bx_2}{Ax_1} + 1\right]^2 \qquad (8)$$

These Van Laar equations can be regarded as empirical versions of equations 3 and 4 where constants A and B are evaluated from experimental data. The relationships between equations 3 and 4, and 7 and 8 are

$$A = V_1(\delta_1 - \delta_2)^2/RT$$

$$A/B = V_1/V_2$$

Van Laar constants, and subsequently activity coefficients and excess free energies of mixing can be evaluated from binary solubility data by the following method suggested by Carlson and Colburn.[11]

At a given temperature the conditions for equilibrium in a two liquid phase system can be expressed by equations 5 and 6. If it is assumed that the Van Laar equations correctly represent activity coefficients as a function of composition, then equations 7 and 8 can be substituted into equations 5 and 6 and the constants A and B can be evaluated. This procedure can be repeated at several temperatures, thereby establishing the temperature dependence of the Van Laar A and B.

The above procedure was used to determine Van Laar constants for several systems of fluorocarbons and hydrocarbons for which the binary solubility data were determined. It was found that in all cases the Van Laar A's and B's were linear functions of temperature as shown in Fig. 7.

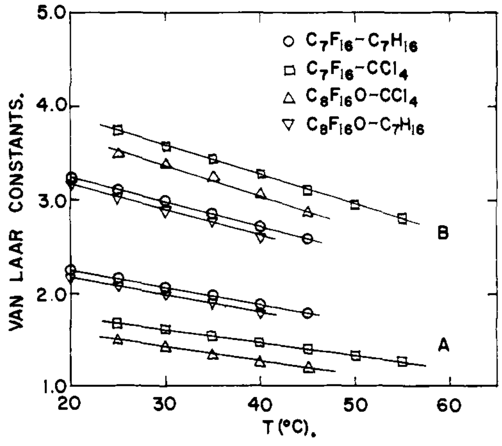

Fig. 7.—Van Laar constants *versus* temperature.

Before activity coefficients calculated from equations 7 and 8 were used, it was necessary to determine their validity. This was done by measur-

---

(10) J. H. Hildebrand and D. R. F. Cochran, THIS JOURNAL, **71**, 22 (1949).

(11) H. C. Carlson and A. P. Colburn, *Ind. Eng. Chem.*, **34**, 581 (1942).

ing the total vapor pressure of the system in the two liquid phase region and comparing this measured pressure with the value calculated from equation 9

$$\pi = x_1p_1^0\gamma_1 + x_2p_2^0\gamma_2 \quad (9)$$

Where p_1^0 and p_2^0 are vapor pressures of components 1 and 2, and π is the total vapor pressure.

Since the total vapor pressure measurements were conducted in the two liquid phase region, the liquid composition could be determined from the temperature and the experimental binary solubility data.

Using the vapor pressure data of components 1 and 2, and the activity coefficients as predicted by the Van Laar equation, the total vapor pressure of the two liquid phase mixture was calculated by equation 9. Values of the total vapor pressure as calculated by equation 9 are plotted *versus* temperature on Fig. 8–13 along with the experimental total vapor pressures for several systems. From Fig. 8–13, it is seen that the Van Laar activity coefficients predict the total vapor pressures fairly accurately in these systems. The agreement between calculated and observed total vapor pressures is seen to be better at lower temperatures.

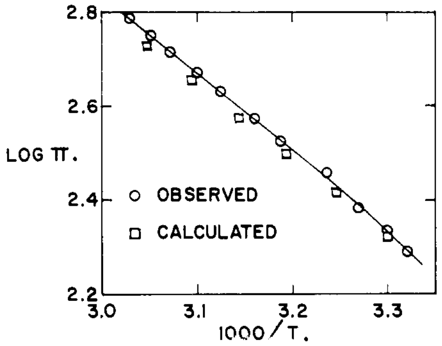

Fig. 8.—Total vapor pressure plot; system perfluoroheptane–carbon tetrachloride.

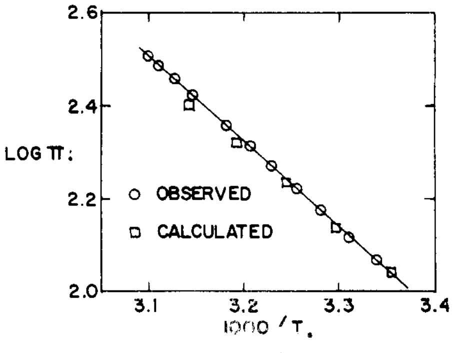

Fig. 9.—Total vapor pressure plot; system perfluoroheptane–*n*-heptane.

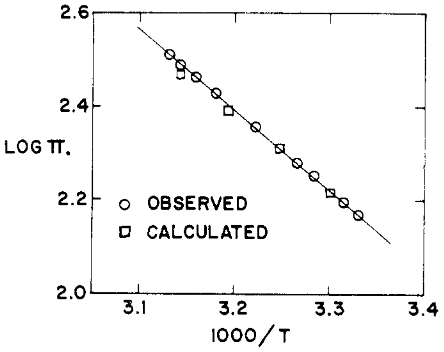

Fig. 10.—Total vapor pressure plot; system perfluorocyclic oxide–carbon tetrachloride.

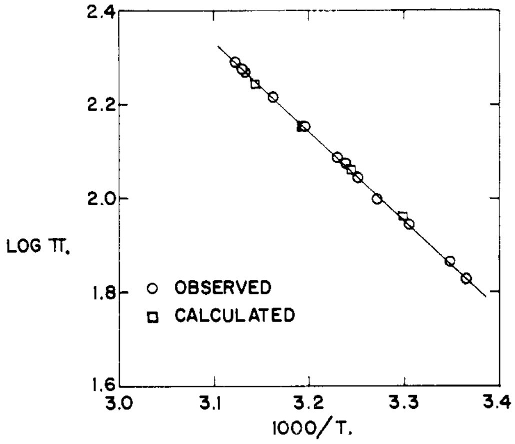

Fig. 11.—Total vapor pressure plot; system perfluorocyclic oxide–*n*-heptane.

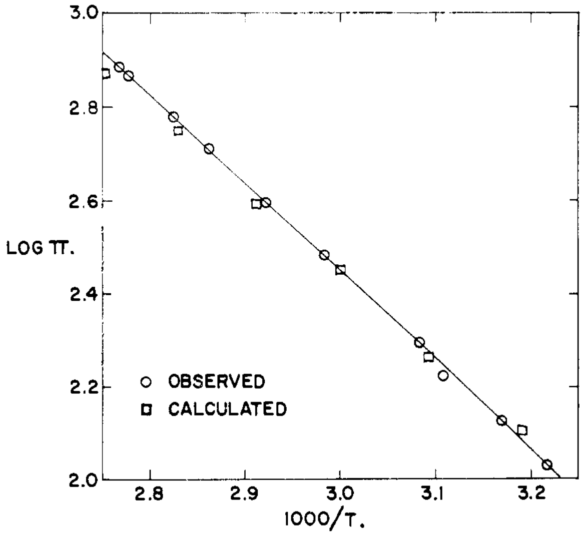

Fig. 12.—Total vapor pressure plot; system perfluorocyclic oxide–toluene.

It is recognized that although the Van Laar activity coefficients can predict the total vapor pressure, this is not definite proof of their validity, since there is an infinite number of combinations of γ_1 and γ_2 which will satisfy equation 9.

As a further check on the validity of the Van Laar activity coefficients, the excess free energies of mixing were calculated from the Van Laar equations using the reported binary solubility data for the systems *n*-pentane–perfluoro-*n*-pentane,[12] *n*-butane–perfluoro-*n*-butane,[13] isoöctane–perfluoroheptane[7] and *n*-hexane–perfluoro-*n*-hexane.[15] Experimental excess free energies have been reported for

---

(12) J. H. Simons and R. D. Dunlap, *J. Chem. Phys.*, **18**, 335 (1950).

(13) J. H. Simons and J. W. Mausteller, *ibid.*, **20**, 1516 (1952).

these systems[12–15] and are compared with the values calculated from the Van Laar equation and binary solubility data in Table V where it can be seen that the two sets of values are in good agreement.

TABLE V

COMPARISON OF ΔF^e CALCULATED BY THE VAN LAAR EQUATIONS WITH LITERATURE VALUES

x_1, mole fraction hydrocarbon	*i*-Octane–perfluoroheptane[16] ΔF^e, cal. mole^{-1} Van Laar	Literature	*n*-Butane–perfluoro-*n*-butane[17] ΔF^e, cal. mole^{-1} Van Laar	Literature	*n*-Pentane–perfluoro-*n*-pentane[18] ΔF^e, cal. mole^{-1} Van Laar	Literature	*n*-Hexane–perfluoro-*n*-hexane[19] ΔF^e, cal. mole^{-1} Van Laar	Literature
0.1	99	128	80	87	87	101		
.2	182	215	147	151	160	181		
.3	246	277	199	203	214	240		
.4	291	315	235	237	255	274		
.5	314	329	253	250	280	295	330	328
.6	311	320	253	247	272	292		
.7	281	290	230	222	248	265		
.8	223	234	182	181	197	217		
.9	131	140	106	112	116	134		

In Table V values of the excess free energy of mixing as calculated by the Van Laar equation are at slightly lower temperatures than the reported literature values. However, in fluorocarbon–hydrocarbon systems, the excess free energy of mixing has not been found to be strongly dependent on temperature since the temperature derivative, the excess entropy of mixing at constant pressure, has been reported[20] to be less than 1 cal. mole^{-1} degree^{-1} at a mole fraction of one half. Since values of the excess free energy of mixing are in the range of 300 cal. mole^{-1} at a mole fraction of one half, a change of 30° would result in less than a 10% change. Because the deviations between observed total vapor pressures and total vapor pressures calculated from the Van Laar equation appear larger at higher temperatures, the excess free energy should be calculated from Van Laar constants determined at lower temperatures in the region of relatively low mutual solubilities.

Excess Free Energy Correlation

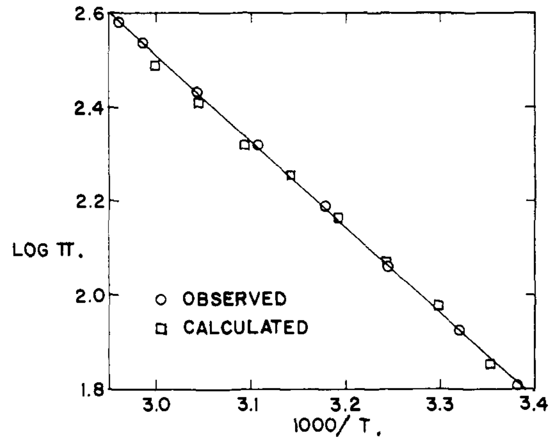

Fig. 13.—Total vapor pressure plot; system perfluorocyclic oxide-methylcyclohexane.

For systems of fluorocarbons and paraffin hydrocarbons it is possible to estimate the excess free energy of mixing or consolute temperature from a knowledge of molal volumes, solubility parameters and ionization potentials of the pure components. The correlation is based on published binary solubility data and excess free energy of mixing data and was established in the following manner.

Reed[21] has shown that by omitting the geometric mean assumption and the assumption of no volume change on mixing the Scatchard–Hildebrand theory accurately predicts heats of mixing in fluorocarbon–hydrocarbon systems. By omitting the geometric mean assumption and retaining the condition of no volume change on mixing the energy of mixing at constant volume ($\Delta E_v{}^M$) can be written

$$\Delta E_v{}^M = (x_1V_1 + x_2V_2)[(\delta_1 - \delta_2)^2 + 2\delta_1\delta_2(1 - f_1f_D)]\phi_1\phi_2$$

in which

$$f_1 = 2(I_1I_2)^{1/2}/(I_1 + I_2) \tag{10}$$

$$f_D = \{2(d_{22}{}^0/d_{11}{}^0)^{1/2}/[1 + d_{22}{}^0/d_{11}{}^0]\}^3$$

and I_1 and I_2 are ionization potentials and $d_{11}{}^0$ and $d_{22}{}^0$ are the distances between centers of nearest-neighbor molecules. An approximation of $d_{22}{}^0/d_{11}{}^0$ can be obtained from the cube root of the molal volume ratio.

Hildebrand[9] has shown that the Helmholtz free energy of mixing at constant volume (ΔA_v) is approximately equal to the Gibbs free energy of mixing at constant pressure (ΔF). If it is further assumed that the excess entropy of mixing at constant volume ($\Delta S_v{}^e$) can be expressed by equation 11, then the excess free energy of mixing is given by equation 12

$$\Delta S_v{}^e = -Z(x_1V_1 + x_2V_2)[(\delta_1 - \delta_2)^2 + 2\delta_1\delta_2(1 - f_1f_D)]\phi_1\phi_2 \tag{11}$$

$$\Delta F^e = (1 + ZT)(x_1V_1 + x_2V_2)[(\delta_1 - \delta_2)^2 + 2\delta_1\delta_2(1 - f_1f_D)]\phi_1\phi_2 \tag{12}$$

Equation 12 can be rewritten to give

$$\Delta F^e = (x_1V_1 + x_2V_2)K\phi_1\phi_2 \tag{12a}$$

where

$$K = (1 + ZT)[(\delta_1 - \delta_2)^2 + 2\delta_1\delta_2(1 - f_1f_D)]$$

Equations 12 and 12a are merely empirical forms of the Scatchard–Hildebrand equation for the excess free energy of mixing. The constant K and subsequently the correlation factor Z was evaluated by fitting equation 12 to published free energy data.

The majority of published data for fluorocarbon–hydrocarbon mixtures, however, is published as

---

(14) C. R. Mueller and J. E. Lewis, *J. Chem. Phys.*, **26**, 286 (1957).

(15) R. G. Bedford and R. D. Dunlap, THIS JOURNAL, **80**, 282 (1958).

(16) Van Laar constants evaluated from solubility data at 17°. Literature values determined from vapor-liquid equilibrium measurements at 30° (ref. 14).

(17) Van Laar constants evaluated from solubility data at 220°K. Literature values were calculated by the authors from reported values of $\Delta\bar{F}_1$ and $\Delta\bar{F}_2$ which were average values determined from vapor-liquid equilibrium measurements in the range of 223 to 260°K. (ref. 13).

(18) Van Laar constants evaluated from solubility data at 262°K. Literature values were calculated by the authors from reported values of $\Delta\bar{F}_1$ and $\Delta\bar{F}_2$ which were average values determined from vapor-liquid equilibrium measurements in the range of 262 to 293°K. (ref. 12).

(19) Van Laar constants evaluated from solubility data at 6°. Literature values determined from vapor-liquid equilibrium measurements at 25° (ref. 15).

(20) A tabulation of these excess entropies for several fluorocarbon-hydrocarbon systems has been reported by R. L. Scott, *J. Phys. Chem.*, **62**, 136 (1958).

(21) T. M. Reed, III, *ibid.*, **59**, 425 (1955).

TABLE VI

DATA USED IN ESTABLISHING EMPIRICAL CORRELATION FOR EXCESS FREE ENERGY

System	Type of data	Temp. °K.	K in eq. 12a and 13	[ ]^a	$Z(10)^3$	Ref.
C_7F_{16}–i-C_8H_{18}	Free energy	303	7.00	3.95	2.54	14
C_7F_{16}–3-$CH_3C_7H_{15}$	Solubility	343	7.67	5.31	1.28	22
C_7F_{16}–n-C_8H_{18}	Solubility	341	6.50	5.86	0.32	23
C_7F_{16}–n-C_7H_{16}	Solubility	328	7.02	5.63	0.76	This work
C_7F_{16}–n-C_6H_{14}	Solubility	302	8.18	4.94	2.18	24
C_7F_{16}–3-$CH_3C_5H_{11}$	Solubility	292	8.12	4.32	3.01	24
C_7F_{16}–2,2$(CH_3)_2C_4H_8$	Solubility	273	6.20	4.34	1.57	24
C_7F_{16}–2,3$(CH_3)_2C_4H_8$	Solubility	283	6.35	4.87	1.06	24
C_5F_{12}–n-C_6H_{14}	Solubility	288	7.45	5.82	0.97	25
C_5F_{12}–2-$CH_3C_5H_{11}$	Solubility	273	7.24	4.15	2.71	25
C_5F_{12}–3-$CH_3C_5H_{11}$	Solubility	278	7.34	3.63	3.67	25
C_5F_{12}–2,2$(CH_3)_2C_4H_8$	Solubility	257	6.92	3.35	4.12	25
C_5F_{12}–2,3$(CH_3)_2C_4H_8$	Solubility	269	7.18	3.94	3.05	25
C_5F_{12}–n-C_5H_{12}	Free energy	266	7.51	4.43	2.63	12
C_4F_{10}–n-C_4H_{10}	Free energy	246	7.72	5.44	1.70	13

^{a}[ ] = $(\delta_1 - \delta_2)^2 + 2\delta_1\delta_2(1 - f_\text{I}f_\text{D})$.

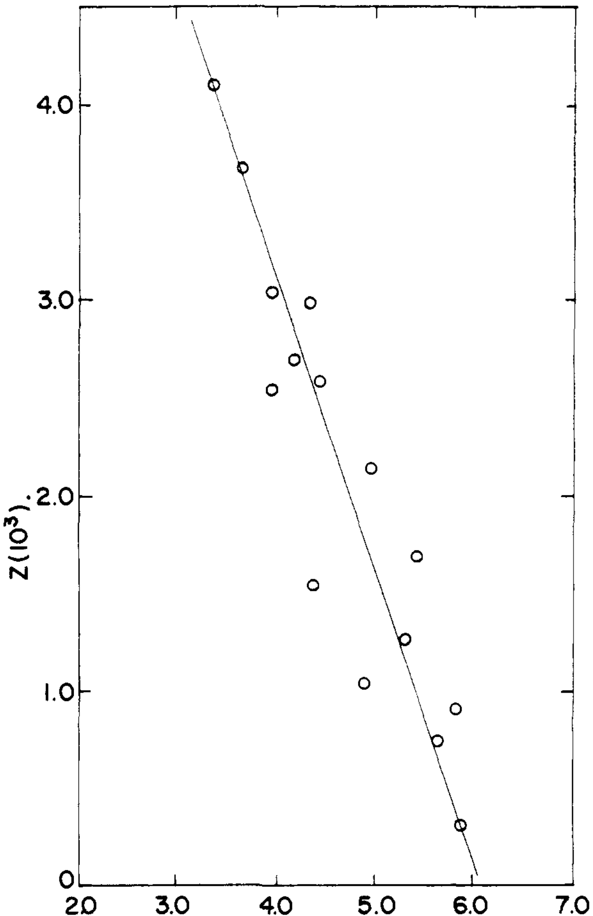

Fig. 14.—Free energy correlation for fluorocarbons and paraffin hydrocarbons.

binary solubility data. For these systems the constant K was determined from a modification of equation 1

$$RT_\text{c} = \frac{2x_1x_2V_1^2V_2^2}{(x_1V_1 + x_2V_2)^3}K \tag{13}$$

Values of the correlation factor Z for fifteen systems are listed in Table VI along with the method of obtaining K. The correlation factor Z is plotted *versus* the quantity $[(\delta_1 - \delta_2)^2 + 2\delta_1\delta_2(1 - f_\text{I}f_\text{D})]$ in Fig. 14. Values of the excess free energy of mixing or consolute temperature can be estimated from Fig. 14 and equations 12 and 13 for systems of fluorocarbons and paraffin hydrocarbons. Systems containing benzene, carbon tetrachloride and chloroform could not be so correlated. Although the experimentally determined values of Z deviate from the correlation line, values of K calculated from the correlation deviate from the experimentally determined K values by an average deviation of 7%, and a maximum deviation of 20%.

Although the correlation is based predominantly on consolute temperature data which are less reliable than free energy data for the evaluation of K,[26] it should be useful as an estimate of the free energy in a fluorocarbon–paraffin hydrocarbon system. It should be noted that this correlation is based on a negative excess entropy of mixing at constant volume.

Test of Free Energy Correlation

This correlation can be used to predict the consolute temperature for the system perfluoro-n-hexane–n-hexane. Data for this system have been published recently by Bedford and Dunlap[15] who found the consolute temperature to be 296°K. Using their reported molal volumes and solubility parameters ($V_1 = 131$, $V_2 = 202$, $\delta_1 = 7.32$, $\delta_2 = 5.88$), the ionization potential of n-hexane[27] ($I_1 = 10.43$), and using the method of Reed[28] to estimate the ionization potential of perfluoro-n-hexane ($I_2 = 17.8$) from the polarizability[29] ($\alpha = 14 \times 10^{-24}$), the calculated value of $[(\delta_1 - \delta_2)^2 + 2\delta_1\delta_{12}(1 - f_\text{I}f_\text{D})]$ was found to be 5.71. Using Fig. 14 the value of Z was found to be 0.58 (10^{-3}). This resulted in a value of $1 + ZT = 1.173$ and $K = 6.71$. Using K equal to 6.71 the consolute temperature as calculated from equation 13 was found to be 290°K. This value compares favorably with the observed value of 296°K. This value of K, however, predicts $\Delta F^\text{c} = 268$ cal. mole^{-1}

---

(22) J. A. Neff and J. B. Hickman, *J. Phys. Chem.*, **59**, 42 (1955).

(23) J. B. Hickman, THIS JOURNAL, **75**, 2879 (1953).

(24) J. B. Hickman, *ibid.*, **77**, 6154 (1955).

(25) R. Dunlap, R. Digman and J. Vreeland, Abstracts of Papers, 124th Meeting American Chemical Society, Chicago, September, 1953.

(26) This fact has been recognized by R. L. Scott, *J. Phys. Chem.* **62**, 136 (1958).

(27) R. E. Honig, *ibid.*, **16**, 105 (1943).

(28) T. M. Reed, III, *ibid.*, **59**, 428 (1955).

(29) J. H. Simons and J. B. Hickman, *ibid.*, **56**, 420 (1952).

at $x = 0.5$, quite a bit lower than the reported value of 328 cal. mole^{-1}. Since it has been noted[26] that values of K calculated from solubility measurements and vapor–liquid equilibrium measurements are sometimes quite different and since the majority of the data used to establish the correlation were solubility data, it is not surprising that the consolute temperature was predicted more accurately than the excess free energy.

Conclusions

Reliable values of the excess free energy of mixing in fluorocarbon–hydrocarbon systems can be calculated from mutual solubility data through the Van Laar equation. Where mutual solubility data are not available, an estimate of the excess free energy of mixing in fluorocarbon–paraffin hydrocarbon systems can be obtained from an empirical correlation if the molal volumes, solubility parameters and ionization potentials of the pure compounds are known.

MANHATTAN, KANSAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Electronic Transitions in Methyl Fluoride and in Fluoroform[1]

BY SUZANNE STOKES[2] AND A. B. F. DUNCAN

RECEIVED MAY 19, 1958

Electronic spectra of CH_3F and of CHF_3 have been obtained in absorption in the vacuum ultraviolet region. The electronic transitions are fitted to series which converge to ionization potentials of the molecules. Vibrational structure associated with two of the transitions is interpreted. A correlation of electronic terms in the series of molecules CH_4, CH_3F, CH_2F_2, CHF_3 and CF_4 is presented.

The electronic energy levels, obtained from a study of vacuum ultraviolet spectra, of a number of halogen derivatives of methane have been reported recently.[3] The present investigation is a continuation of this work, and the vacuum ultraviolet absorption spectra of CH_3F and CHF_3 are presented here.

Experimental Details

The CH_3F was obtained from Dr. W. F. Edgell of Purdue University. He reported that the infrared spectrum of the compound showed that no impurities were present. Another sample of CH_3F was prepared following the procedure given by Edgell.[4] A mass spectrographic analysis indicated that the second sample contained about 0.05% of an impurity which had a mass of 28. This impurity was probably nitrogen or possibly ethylene.

Fluoroform was obtained from the Kinetic Chemicals Division of du Pont de Nemours Company, who stated that the sample showed no impurities by mass spectrographic analysis. This statement was confirmed independently by a mass spectrum determined here.

The spectra were photographed in the first order of a vacuum grating spectrograph.[5] The grating, of one meter radius of curvature, was ruled 30,000 lines per inch on a two inch surface, and was mounted at about normal incidence. The dispersion was equal to about 8.32 Å./mm. The slit was about 0.1 mm. wide. Eastman Kodak Company SWR film was used.

Most of the spectra appeared at very low pressures. In such cases the vapor was introduced directly into the spectrograph through calibrated volumes to a known pressure and was separated from the background source only by the slit. The light source was operated at about 0.5 mm. of He, and while some He diffused through the slit, none of the absorbing gas was lost during an exposure.

The Lyman continuum was used as a background for absorption spectra. It was operated by periodic discharge, once a second, of a one microfarad capacitor, charged to about 15,000 volts. Helium gas at a pressure of about 0.5 mm. was used as a carrier gas. Narrow emission lines of carbon, silicon and atomic oxygen[6] occurring in this source were used as wave length standards. The continuum was satisfactory except in the region 1000 to 840 Å. where the strongest absorption of oxygen occurs. This oxygen probably originated from decomposition of quartz vapor from the capillary where the discharge occurred and could not be eliminated. This region in the methyl fluoride spectrum was investigated in detail with a hollow cathode copper discharge. The numerous well resolved lines of the Cu I[7] spectra in this source allowed a point by point plot of the contours of absorption in this region which was shown to be continuous.

To investigate the possibility of weak absorption at longer wave lengths than about 1300 Å., pressures greater than 0.5 mm. of absorbing gas were required. For this purpose an uncondensed discharge in hydrogen was used, separated from the absorbing gas in the spectrograph by a LiF window. Absorption coefficients in this region were determined at wave lengths of lines in the hydrogen molecular spectrum.

Intensity maxima of broad continuous bands were measured from microphotometer tracings. The estimated error in these measurements was about 5 to 8 Å. When hydrogen lines or copper lines served as the background, band envelopes were found by plotting the absorption coefficients against wave lengths. The band maxima were read from these curves to about 5 to 10 Å., depending on the breadth near the maximum. For sharp vibrational bands the error in measurement was about 10 cm.$^{-1}$.

Description of Spectra

The observed electronic transitions in the two molecules are shown in Fig. 1, where relative intensities, derived principally from appearance pressures are plotted against wave number. Further details are reported below concerning the behavior of the transitions with change of pressure.

Methyl Fluoride.—This molecule was studied over the pressure range of 0.003 to 2.6 mm. The spectrum consisted of five electronic transitions, one

---

(1) Part of a dissertation submitted by Suzanne Stokes to the Graduate School of the University of Rochester in partial fulfillment for the requirements of the degree of Doctor of Philosophy. This work was supported in part by the Office of Ordnance Research, U. S. Army, under contract DA-30-115-ORD-728(620) with the University of Rochester. Reproduction in whole or in part is permitted for any use of the U. S. Government.

(2) Eastman Kodak Company Fellow, 1956–1957.

(3) C. R. Zobel and A. B. F. Duncan, THIS JOURNAL, **77**, 2611 (1955). Reference to previous work on related molecules will be found in this reference.

(4) W. F. Edgell and L. Parts, *ibid.*, **77**, 4899 (1955).

(5) G. Moe and A. B. F. Duncan, *ibid.*, **74**, 3136 (1952).

(6) J. C. Boyce and J. T. Moore, "Provisional Wavelength Identification for Vacuum Ultraviolet," Massachusetts Institute of Technology, 1941.

(7) A. G. Shenstone, *Phil. Trans. Roy. Soc.*, **A235**, 195 (1936).