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Technology-Gaseous
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MISCELLANEOUS STUDIES OF FLUOROCARBONS AND FLUOROCARBON- URANIUM HEXAFLUORIDE SYSTEMS

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MISCELLANEOUS STUDIES OF FLUOROCARBONS AND FLUOROCARBON-URANIUM
HEXAFLUORIDE SYSTEMS

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A B S T R A C T

During the exploration of the possible use of an extraction process for the separation of gaseous cascade impurities from uranium hexafluoride, a number of short exploratory studies were carried out. These included (1) experimental determination of the vapor pressure and liquid density of perfluorodibutylcyclicether, (2) calculation of the liquid vapor-equilibria of the systems perfluoro-n-pentane-uranium hexafluoride and 1,2-dichlorohexafluoropropane-uranium hexafluoride, and (3) derivation of equations for the estimation of activity coefficients in ternary systems from the properties of the pure components. The results of these studies are summarized in this report.

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MISCELLANEOUS STUDIES OF FLUOROCARBONS AND FLUOROCARBON-
URANIUM HEXAFLUORIDE SYSTEMS

Several fluorocarbons were investigated and rejected for possible use in an extraction process for the separation of nitrogen and uranium hexafluoride. The purpose of this report is to record such experimental data and phase calculations as are considered to be of possible future use. These include (1) the experimental vapor pressure and liquid density of a perfluorocyclicether having desirable volatility characteristics, (2) the calculated liquid-vapor equilibrium for the system perfluoro-n-pentane-uranium hexafluoride, (3) a rough calculation of the liquid-vapor equilibrium for the system 1,2-dichlorohexafluoropropane-uranium hexafluoride, and (4) a method for calculating activity coefficients for use in the prediction of phase equilibria in ternary systems.

VAPOR PRESSURE AND LIQUID DENSITY OF PERFLUORODIBUTYLCYCLICETHER

The vapor pressure and liquid density of a perfluorocyclicether were determined experimentally. The empirical formula of this compound is $C_8F_{16}O$, and its molecular weight is 416.25, but its exact structure is unknown. It is made by Minnesota Mining and Manufacturing Company.

Experimental Procedure

Vapor Pressure Apparatus. A dynamic type apparatus was used for the vapor pressure determination. The boiler was designed so that boiling liquid spouted out of a small tube onto the thermocouple well. The temperature was measured by a calibrated iron-constantan thermocouple and a potentiometer. The vapor over the boiling liquid rose to a reflux condenser at which point the pressure was balanced by a blanket of nitrogen. The nitrogen pressure was measured with a mercury manometer. Corrections were made for the thermal expansion of the mercury.

Density. A plumb bob of known weight and volume was immersed in the sample of perfluorocyclicether. The bob was suspended from the arm of an analytical balance by means of a fine wire. The sample was contained in a large test tube which was immersed in water inside a Dewar flask. The density was calculated from the change of weight of the plummet when suspended in the liquid. Corrections were made for the thermal expansion of the plummet.

Results

The raw vapor pressure and density data are given in tables I and II respectively. These data were correlated by the following equations:

$$\log P = 7.72115 - \frac{1657.09}{t + 241.04} \quad (1)$$

$$\text{and} \quad \rho = 1.828 - 2.48 \times 10^{-3}t - 1.9 \times 10^{-6}t^2 \quad (2)$$

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TABLE I

VAPOR PRESSURE OF PERFLUORODIBUTYLCYCLICETHER

Temperature, °C.	Vapor Pressure, Experimental, mm. of Hg	Vapor Pressure, Calc. Eq. 1, mm. of Hg
32.6	46.7	46.3
32.9	47.2	47.0
35.6	53.5	53.8
38.0	60.8	60.6
52.6	121.6	119.6
63.8	194.0	192.9
64.4	198.7	197.7
69.9	247.7	246.5
81.9	389.4	388.9
100.8	752.5	747.5
101.7	767.9	769.7
106.0	883.8	883.5

TABLE II

DENSITY OF PERFLUORODIBUTYLCYCLICETHER

Temperature, °C.	Density, Experimental, g./cc.	Density, Calc. Eq. 2, g./cc.
-78.75	2.0135	2.035
-11.13	1.8536	1.855
0	1.8313	1.828
15.90	1.7873	1.789
40.54	1.7250	1.725
62.13	1.6649	1.667
64.56	1.6596	1.660

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where P is the vapor pressure in mm. of mercury,
 ρ is the density in g. per cc.,
 and t is the temperature in degrees Centigrade.

Table III contains smoothed values of the vapor pressure and density as well as various values calculated for use in the estimation of activity coefficients by the method of Hildebrand, Scatchard, Flory, and Huggins (3,4,6,8,9,11). Further work was not done since other compounds appeared to be more promising for the immediate problem at hand.

LIQUID-VAPOR EQUILIBRIUM OF THE SYSTEM PERFLUORO-N-PENTANE-URANIUM HEXAFLUORIDE

Interest in perfluoro-n-pentane as a possible extractant arose because of the occasional presence in the gas stream of moderately low boiling materials such as chlorine trifluoride, fluorine oxychlorides, and Freon-114 which would have to be separated from the uranium hexafluoride in an auxiliary column if an extractant having a higher boiling point than uranium hexafluoride were used. Perfluoro-n-pentane boils at 29.2°C. (1) which is intermediate between the uranium hexafluoride and the impurities, so that the impurities would be removed with the distilling solvent and the use of a second column would be avoided. In order to obtain an idea of the nature of the liquid-vapor equilibrium in the perfluoro-n-pentane-uranium hexafluoride system, the liquid-vapor equilibrium has been evaluated from the activity coefficients of Hildebrand and Wood, Scatchard, Flory and Huggins (3,4,6,8,9,11) and the techniques discussed by the authors (2) in an earlier report.

The following equations for the vapor pressure, P , and the liquid density, ρ , of perfluoro-n-pentane were obtained from the literature (1).

$$\log P = 6.88375 - \frac{961.192}{T} - \frac{75512.4}{T^2} \quad (1)$$

where T is the temperature in degrees Kelvin,
 and P is the vapor pressure in millimeters.

$$\rho = 1.6832 - 3.1158 \times 10^{-3}t - 3.16 \times 10^{-6}t^2 \quad (2)$$

where t is the temperature in degrees centigrade,
 and ρ is the density in g./cc.

Using these equations and ordinary thermodynamics and equations of state, the following equations necessary for the evaluation of the activity coefficients were developed.

$$V_1 = \frac{0.288}{\rho} \quad (3)$$

$$V_v = \frac{RT}{P + \frac{12114}{(RT/P)^2}} + 0.1302 \quad (4)$$

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TABLE III

PHYSICAL AND THERMODYNAMIC PROPERTIES OF PERFLUORODIBUTYLCYCLICETHER

Temperature, °C.	Vapor Pressure*, mm. of Hg	Liquid Molar Volume**, cc./mole	Vapor Molar Volume***, cc./mole	Heat of Vaporization, cal./mole	Internal Energy of Vaporization, cal./mole	δ -Function, $(\frac{\text{cal.}}{\text{mole cc.}})^{1/2}$
-100	0.000094	202.35	1.152×10^{11}	11432	11088	7.402
- 75	0.0055	207.81	2.244×10^{19}	10803	10409	7.077
- 50	0.1115	213.79	1.249×10^8	10352	9908	6.808
- 25	1.124	220.35	1.377×10^8	10004	9511	6.570
0	7.021	227.71	2.427×10^6	9738	9196	6.355
25	31.08	235.84	598444	9522	8929	6.153
50	106.5	245.00	189153	9331	8690	5.956
75	300.5	255.21	72259	9196	8479	5.764
100	728.2	266.66	31813	8960	8228	5.555
125	1563	279.74	15727	8722	7953	5.332
150	3044	294.59	8479	8400	7604	5.080

*Calculated from equation 1

**Calculated from the density as determined by equation 2

***Allowance was made for the non-ideal nature of the vapor

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$$\Delta H_v = \frac{P\Delta V}{T} \frac{d \ln P}{d(\frac{1}{T})} = (2213.6 + \frac{347810}{T}) \frac{P(V_v - V_l)}{T} \quad (5)$$

$$\Delta E_v = \Delta H_v - 3.185 \times 10^{-5} P(V_v - V_l) \quad (6)$$

$$\delta = \left(\frac{\Delta E_v}{1000 V_l} \right)^{1/2} \quad (7)$$

where V_l and V_v are the molar volumes of liquid and vapor perfluoro-n-pentane respectively in liters per mole,

R is the ideal gas constant, 62.362, in liter-millimeters deg.⁻¹ mole⁻¹,

ΔH_v is the heat of vaporization in calories per mole,

ΔE_v is the internal energy of vaporization in calories per mole,

$\left(\frac{\Delta E}{1000 V_l} \right)$ is called the cohesive energy density,

and $\left(\frac{\Delta E_v}{1000 V_l} \right)^{1/2}$ is called the δ -function.

These results are tabulated in table IV.

The necessary data for uranium hexafluoride were obtained from previous papers (2,10). The calculated activity coefficient, phase compositions, and total pressures for the liquid-vapor equilibrium of the system perfluoro-n-pentane-uranium hexafluoride at 60, 70, 80, and 90°C. are presented in tables V, VI, VII, and VIII. The calculations indicate that an azeotrope containing about 20 mole per cent uranium hexafluoride is formed. This means that because the calculation for systems of this type is generally conservative, azeotrope formation is not an absolute certainty, but, at best, the separation would be extremely difficult to perform.

LIQUID-VAPOR EQUILIBRIUM OF THE SYSTEM URANIUM HEXAFLUORIDE- 1,2-DICHLOROHEXAFLUOROPROPANE

The boiling point, 34.7°C., and chemical composition of 1,2-dichlorohexafluoropropane, $\text{CF}_2\text{Cl}-\text{CFCl}-\text{CF}_3$, are such that this compound is of interest as a possible extractant for uranium hexafluoride in the system proposed for the purge cascade of a gaseous diffusion plant. Since the boiling point and the liquid density at 20°C., 1.5896 g./ml., were the only available data (5) the vapor pressure at 20°C. and the heat of vaporization were estimated from the known properties of Freon-114 and the rules for the behavior of members of a homologous series. Using these estimated values and the known density and molecular weight, a liquid-vapor equilibrium composition isotherm was calculated by the method of Hildebrand, Scatchard, Flory and Huggins (3,4,6,8,9,11). The results are given in table IX. The

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TABLE IV

THE PHYSICAL AND THERMODYNAMIC PROPERTIES OF PERFLUORO-N-PENTANE

Temperature, °C.	Vapor Pressure, mm. of Hg	Molar Volume, liters		Heat of Vaporization, ΔH_v cal./mole	Energy of Vaporization, ΔE_v cal./mole	δ -Function, $\left(\frac{\text{cal.}}{\text{mole cc.}}\right)^{1/2}$
		Liquid	Vapor			
0	226	0.1711	74.85	6.870	6.332	9.006
10	353	0.1744	49.46	6.735	6.181	8.825
20	533	0.1778	33.80	6.620	6.049	8.716
30	780	0.1815	23.74	6.486	5.901	8.550
40	1109	0.1854	17.14	6.358	5.759	8.414
50	1537	0.1900	12.67	6.220	5.609	8.260
60	2084	0.1940	9.550	6.071	5.450	8.081
70	2767	0.1987	7.339	5.917	5.288	7.930
80	3606	0.2037	5.733	5.751	5.116	7.742
90	4622	0.2091	4.549	5.578	4.939	7.550

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TABLE V

LIQUID-VAPOR EQUILIBRIUM OF THE SYSTEM PERFLUORO-N-PENTANE-URANIUM
HEXAFLUORIDE AT 60°C.

Mole fraction of UF ₆ in Liquid	Activity Coefficient, γ of UF ₆	Activity Coefficient, γ of n-C ₅ F ₁₂	Molar Fraction of UF ₆ in Vapor	Total, Pressure, mm. of Hg
0.00	-----	1.000	0.00	2084
0.01	2.508	1.000	0.012	2088
0.05	2.420	1.001	0.058	2103
0.10	2.313	1.005	0.109	2116
0.20	2.103	1.022	0.198	2124
0.40	1.712	1.120	0.328	2084
0.60	1.373	1.404	0.413	1994
0.80	1.116	2.324	0.480	1861
0.90	1.034	3.624	0.552	1685
0.95	1.009	4.862	0.653	1467
1.00	1.000	-----	1.000	999*

*Extrapolated from the vapor pressure curve for uranium hexafluoride

TABLE VI

LIQUID-VAPOR EQUILIBRIUM OF THE SYSTEM PERFLUORO-N-PENTANE-URANIUM
HEXAFLUORIDE AT 70°C.

Mole Fraction of UF ₆ in Liquid	Activity Coefficient, γ of UF ₆	Activity Coefficient, γ of n-C ₅ F ₁₂	Mole Fraction of UF ₆ in Vapor	Total Pressure, mm. of Hg
0.00	-----	1.000	0.00	2767
0.01	2.445	1.000	0.012	2773
0.05	2.365	1.001	0.058	2794
0.10	2.264	1.005	0.110	2812
0.20	2.066	1.021	0.200	2827
0.40	1.692	1.116	0.334	2779
0.60	1.366	1.391	0.421	2662
0.80	1.114	2.278	0.492	2482
0.90	1.033	3.529	0.566	2250
0.95	1.009	4.738	0.667	1969
1.00	1.000	-----	1.000	1370

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TABLE VII

LIQUID-VAPOR EQUILIBRIUM OF THE SYSTEM PERFLUORO-N-PENTANE-URANIUM
HEXAFLUORIDE AT 80°C.

Mole Fraction of UF ₆ in Liquid	Activity Coefficient, γ of UF ₆	Activity Coefficient, γ of n-C ₅ F ₁₂	Mole Fraction of UF ₆ in Vapor	Total Pressure, mm. of Hg
0.00	-----	1.000	0.00	3606
0.01	2.332	1.000	0.012	3613
0.05	2.259	1.001	0.057	3637
0.10	2.169	1.004	0.109	3659
0.20	1.990	1.020	0.199	3674
0.40	1.650	1.108	0.336	3612
0.60	1.347	1.366	0.430	3457
0.80	1.110	2.187	0.509	3210
0.90	1.032	3.328	0.587	2908
0.95	1.009	4.421	0.689	2560
1.00	1.000	-----	1.000	1840

TABLE VIII

LIQUID-VAPOR EQUILIBRIUM OF THE SYSTEM PERFLUORO-N-PENTANE-URANIUM
HEXAFLUORIDE AT 90°C.

Mole Fraction of UF ₆ in Liquid	Activity Coefficient, γ of UF ₆	Activity Coefficient, γ of n-C ₅ F ₁₂	Mole Fraction of UF ₆ in Vapor	Total Pressure, mm. of Hg
0.00	-----	1.000	0.00	4622
0.05	2.163	1.001	0.017	4657
0.10	2.082	1.004	0.108	4681
0.20	1.922	1.019	0.198	4697
0.40	1.611	1.101	0.338	4614
0.60	1.330	1.342	0.438	4414
0.80	1.105	2.103	0.524	4086
0.90	1.031	3.148	0.607	3702
0.95	1.008	4.139	0.708	3277
0.99	1.000	5.394	0.906	2648
1.00	1.000	-----	1.000	2422

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TABLE IX

PRESSURE-COMPOSITION EQUILIBRIUM ISOTHERM OF THE SYSTEM:
 URANIUM HEXAFLUORIDE-1,2-DICHLOROHEXAFLUOROPROPANE

<u>Mole Fraction of UF₆ in Liquid</u>	<u>Mole Fraction of UF₆ in Vapor</u>	<u>Total Pressure, mm. of Hg</u>	<u>Activity Coefficient of UF₆ in Liquid</u>	<u>Activity Coefficient of C₃Cl₂F₆ in Liquid</u>
0	0	456.6	-----	1.000
0.10	0.084	458	1.777	1.002
0.20	0.158	446	1.631	1.008
0.40	0.284	422	1.380	1.082
0.60	0.384	379	1.119	1.252
0.80	0.544	336	1.052	1.644
0.90	0.669	296	1.014	2.101
1.00	1.000	217	1.000	-----

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greater part of this curve is hypothetical since the solution would be supersaturated at uranium hexafluoride concentrations greater than 24 mole per cent; however, the extrapolation of the density and vapor pressure to temperatures as high as 64°C., the triple point of uranium hexafluoride, would be very uncertain and the results less reliable than those obtained at 20°C.

The fact that no azeotrope was predicted at 20°C. indicates that probably none would occur at higher temperatures. Since there is no known commercial source of this compound, no further work was carried out.

PREDICTION OF PHASE EQUILIBRIA IN TERNARY SYSTEMS

Because two different coolants are now being used in the gaseous diffusion plant, methods of evaluating ternary systems involving uranium hexafluoride and fluorocarbons or chlorofluorocarbons are of increasing importance. Although the traditional experimental techniques for obtaining liquid-vapor and solid-liquid equilibria may be employed, these are both costly and time consuming. Frequently, the design engineer only requires data of sufficient accuracy to establish the desirability of trying a certain process. The use of traditional techniques for this purpose is usually impractical since obtaining the necessary phase equilibria data ordinarily require more time than is available for the evaluation of the whole process. For the ternary solution of unassociated, non-polar molecules having similar degrees of interpenetration (i.e., uranium hexafluoride, fluorocarbons, and chlorofluorocarbons), formulations for the binary systems have been developed which predict with reasonable accuracy the gross behavior of the system. These formulations can be extended to ternary systems in order to predict their general behavior. Although the accuracy is further reduced in ternary systems over what it is with binary systems, the computations are still useful in obtaining an idea of the general behavior of a ternary system for design purposes. Using the generalized treatment of Hildebrand and Wood (6) and Scatchard (11) for the effect of differences in "internal pressures" or "cohesive energy densities" upon the excess energy of mixing and the generalized treatment of Hildebrand (7) for the excess entropy of mixing of unequal size, one obtains the following equation for the activity coefficient of component 1 in a ternary solution in terms of the physical properties of the pure components.

$$RT \ln \gamma_1 = V_1 \left\{ (\delta_1 - \delta_2)^2 \phi_2^2 + (\delta_1 - \delta_3)^2 \phi_3^2 + [(\delta_1 - \delta_2)^2 + (\delta_1 - \delta_3)^2 - (\delta_2 - \delta_3)^2] \phi_2 \phi_3 \right\} + RT \left[\ln \frac{\phi_1}{X_1} - \phi_2 \left(\frac{V_1}{V_2} - 1 \right) - \phi_3 \left(\frac{V_1}{V_3} - 1 \right) \right] \quad (8)$$

where X_1 , X_2 , and X_3 are the mole fractions of components 1, 2, and 3 respectively,

ϕ_1 , ϕ_2 , and ϕ_3 are the volume fractions of components 1, 2, and 3 respectively,

$$\phi_1 \text{ being defined as } \frac{X_1 V_1}{X_1 V_1 + X_2 V_2 + X_3 V_3}$$

V_1 , V_2 , and V_3 are the molar volumes in ml. of components 1, 2, and 3 respectively,

δ_1 , δ_2 , and δ_3 are the delta functions of components 1, 2, and 3 and are defined as

$$\delta_1 = \left(\frac{\Delta E_1^v}{V_1} \right)^{1/2}, \delta_2 = \left(\frac{\Delta E_2^v}{V_2} \right)^{1/2}, \text{ and } \delta_3 = \left(\frac{\Delta E_3^v}{V_3} \right)^{1/2}$$

ΔE_1^v , ΔE_2^v , and ΔE_3^v are the molar energies of vaporization of components 1, 2, and 3 in calories per mole,

$\frac{\Delta E_1^v}{V_1}$, $\frac{\Delta E_2^v}{V_2}$, and $\frac{\Delta E_3^v}{V_3}$ are known as the "internal pressures" or "cohesive energy densities" of components 1, 2, and 3 respectively,

R is the gas constant in calories per mole per degree Kelvin, and T is the temperature in degrees Kelvin.

Suitable changes in the subscripts in equation 8 give the activity coefficients of components 2 and 3. The phase relations and diagrams may then be developed by the use of the appropriate equations.

Although these equations have not yet been used for calculations of equilibria in ternary systems, they are available and are applicable to systems such as Freon-114-C-816-uranium hexafluoride, chlorine trifluoride-C-816-uranium hexafluoride and trichloropentafluoropropane-C-816-uranium hexafluoride.

SUMMARY

1. The vapor pressure and liquid density of perfluorodibutylcyclicether are given by the following equations:

$$\log P = 7.72115 - \frac{16507.09}{t+241.04}$$

$$\text{and } \rho = 1.828 - 2.48 \times 10^{-3}t - 1.9 \times 10^{-6}t^2$$

where P is the vapor pressure in mm. of mercury,
 ρ is the density in g./cc.,
 and t is the temperature in °C.

2. The calculated liquid-vapor equilibria for the system perfluoro-n-pentane-uranium hexafluoride predict the formation of a minimum boiling azeotrope containing about 20 mole per cent uranium hexa-

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fluoride. Because the calculation for systems of this type is generally conservative, azeotrope formation is not an absolute certainty; but, at best, the separation would be very difficult.

3. Rough calculations indicate that the compound, perfluoro-1,2-dichlorohexafluoropropane, is probably separable from uranium hexafluoride and would possibly be useful if an extractant having a boiling point between that of uranium hexafluoride and those of materials such as chlorine trifluoride and the chlorine oxides is required.
4. Equations expressing the activity coefficients of the components of a ternary system in terms of the properties of the pure components have been derived.

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BIBLIOGRAPHY

1. Barber, E. J., The Liquid-Vapor Equilibrium of the System Tungsten Hexafluoride-Perfluoro-n-Pentane and Some Related Studies, Thesis, University of Washington (December, 1948).
2. Barber, E. J., Posey, J. C., and Junkins, J. H., Phase Equilibria of the System Uranium Hexafluoride-Freon-114, Carbide and Carbon Chemicals Company, K-25 Plant, to be issued (K-1075).
3. Flory, P. J., "Thermodynamics of High Polymer Solutions", J. Chem. Phys., 9, 660 (1941); Ibid., 10, 51 (1942).
4. Flory, P. J., "Thermodynamics of Dilute Solutions of High Polymers", J. Chem. Phys., 13, 453-65 (1945).
5. Gabbard, J. L., Gibson, J. D., Faloon, A. V., Rapp, K. E., Frey, S. E., and Walker, D. V., Fluorocarbons and Fluoroorganic Compounds, Section II, Carbide and Carbon Chemicals Company, K-25 Plant, August 2, 1948 (K-220).
6. Hildebrand, J. H. and Wood, S. E., "The Derivation of Equations for Regular Solutions", J. Chem. Phys., 1, 817 (1933).
7. Hildebrand, J. H., "The Entropy of Solution of Molecules of Different Sizes", J. Chem. Phys., 15, 225 (1947).
8. Huggins, M. L., "Solutions of Long Chain Compounds", J. Chem. Phys., 9, 440 (1941).
9. Huggins, M. L., "Some Properties of Solutions of Long-Chain Compounds", J. Phys. Chem., 46, 151 (1942).
10. Jordan, G. S., Posey, J. C., and Rutledge, G. P., Liquid-Vapor and Solid-Liquid Equilibria of the System Uranium Hexafluoride-Perfluorotributylamine, Carbide and Carbon Chemicals Company, K-25 Plant, October 28, 1953 (K-1073).
11. Scatchard, G., "Equilibria in Non-Electrolyte Solutions in Relation to the Vapor Pressures and Densities of the Components", Chem. Revs., 8, 321 (1931).

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