

A similar analysis of the data given by Gopal and Husain (6) for the solubility of these six salts in formamide has been carried out. The constants in Equation 1 were determined by the method of least squares and the heat of solution at 25° C. determined in the same way as that used above for *N*-methyl formamide solutions. The results are shown in Table III. Again it can be seen that the heats of solution are very small. It must be pointed out, however, that there is not good agreement between the results calculated here and those obtained by a direct calorimetric method by Mishchenko and Sukhotim (13) in formamide in those cases where comparison is possible. However, this lack of agreement may result from our assumption that the activity coefficient does not change with temperature. The results in both cases indicate that the heats of solution are quite small.

LITERATURE CITED

- (1) Berger, C., Dawson, L.R., *Anal. Chem.* **24**, 994 (1952).
- (2) Bordwell, F.G., "Organic Chemistry," p. 446, Macmillan, N. Y., 1963.
- (3) D'Alelio, G.F., Reid, E.E., *J. Am. Chem. Soc.* **59**, 109 (1937).
- (4) Dawson, L.R., Berger, J.E., Vaughn, J.W., Eckstrom, H.C., *J. Phys. Chem.* **67**, 281 (1963).
- (5) French, C.M., Glover, K.H., *Trans. Faraday Soc.* **51**, 1418 (1955).
- (6) Gopal, R., Husain, M.M., *J. Indian Chem. Soc.* **40**, 272 (1963).
- (7) Handbook of Chemistry and Physics, Hodgman, C.D., ed., 40 ed., p. 2512, Chemical Rubber, Cleveland, 1958.
- (8) Harned, H.S., Owen, B.B., "The Physical Chemistry of Electrolytic Solutions," 3rd ed., p. 77, Reinhold, N. Y., 1958.

Table III. Constants in Equation 1 for the Solubilities as a Function of Temperature for Salts in Formamide

Calculated from data given by Gopal and Husain (6). Heats of solution were calculated from the solubility data assuming that the activity coefficient does not vary with temperature.

Salt	A	B	$m_{ss}^{(298)}_{\text{calcd.}}$	$H^* - H_{298}^{\Delta}$ Kcal./Mole
NaCl	-0.006074	3.3968	1.586	-1.354
NaBr	0.03095	-5.7337	3.496	3.129
KCl	0.002057	0.2279	0.841	0.864
KBr	0.002606	1.0244	1.802	0.511
NH ₄ Cl	0.01306	-1.8334	2.061	2.240
NH ₄ Br	0.01714	-1.4253	3.686	1.644

- (9) Heilbron, I.M., ed., Dictionary of Organic Compounds, p. 709, Oxford University Press, N. Y., 1953.
- (10) International Critical Tables, Washburn, E.W., ed., vol. IV, pp. 218, 235, 239, McGraw-Hill, N. Y., 1928.
- (11) Leader, G.R., *J. Am. Chem. Soc.* **73**, 856 (1951).
- (12) Leader, G.R., Gormley, J.F., *Ibid.* **73**, 5731 (1951).
- (13) Mishchenko, K.P., Sukhotim, A.M., *Dokl. Akad. Nauk SSSR* **98**, 103 (1954).
- (14) Sisler, H.H., "Chemistry in Non-aqueous Solvents," p. 31, Reinhold, N. Y., 1961.
- (15) Williams, A.T., *Trans. Faraday Soc.* **40**, 421 (1944).
- (16) Wyman, J., Jr., Ingalls, E.N., *J. Am. Chem. Soc.* **60**, 1182 (1938).

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Vapor Pressure of Liquid Methanol at Low Temperatures

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The vapor pressure of liquid CH₃OH was measured near the melting point. The results were used in a third law calculation to test the consistency of various thermodynamic data for the liquid and vapor. The most apparent uncertainty lies in the equation of state of the vapor.

FROM X-RAY diffraction studies of crystalline methanol at low temperatures (11, 18) it is known that there is no residual entropy from random hydrogen bonding such as occurs in the related case of ice. However, the spectroscopic entropy value was not brought into reasonable agreement with the calorimetric value until it was first shown that methanol vapor is exceedingly nonideal (19). Even then the problem was compounded by the presence of a transition in the solid inconveniently close to the melting point,

by some remaining uncertainty in the value of the barrier to internal rotation, and by the fact that not all of the normal frequencies could be identified from the vibrational spectrum. Recent work has surmounted these difficulties. Thus, the heat capacity of the solid and liquid has been remeasured with considerable care (2), the barrier to internal rotation is accurately known from the microwave spectrum (7), and the vibrational assignment has been all but settled through normal coordinate analyses (3, 12, 20).

Also, the equation of state has been redetermined (10). The thermodynamic functions of the liquid and the hypothetical ideal vapor are now known, therefore, to a high degree of accuracy below the boiling point. Because of the difficulties associated with the determination of the equation of state, the same cannot be assumed for the real vapor, even at moderate pressures.

The vapor pressure of liquid methanol near the melting point was measured in this laboratory. The results were combined with the well-established values above 10 mm. of Hg (1) in a third law calculation. In another third law calculation heat of vaporization data were used to obtain the difference between the spectroscopic and calorimetric entropies. Although the internal consistency proved to be good in these calculations, some uncertainty was indeed apparent in the real gas correction terms.

EXPERIMENTAL

The vapor pressure of methanol was measured at seven temperatures with a Knudsen gage and procedure described earlier (14). The accuracy of the gage as a manometer was estimated at $\pm 3\%$. The scatter in the vapor pressure data was $\pm 6\%$ when based on the thermodynamic analysis presented in Table I and resulted mainly from momentary adsorption or desorption of methanol vapor inside the gage caused by small temperature fluctuations of the gage heater. Of particular importance was the fact that the gage had been calibrated against the known vapor pressures of ice, benzene and carbon tetrachloride at low temperatures. The vapor pressures of these three substances could be accurately extrapolated from room temperature (13). In this way the usual calibration against a McLeod gage was avoided. Recent studies show that results using the McLeod gage are subject to serious errors. This is probably due to the pumping action of mercury vapor streaming into the isolating cold trap (6, 14, 17).

Table I. Heat of Sublimation of Methanol at Absolute Zero Based on Vapor Pressure

T, ° K.	Cal./Mole	
	$-RT \ln f/P$	$\Delta H_{\text{sub}}^{\circ}$
	This Work	
175.04	0	10900
175.58	0	10910
176.46	0	10924
177.12	0	10901
178.11	0	10910
179.05	0	10901
180.25	0	10882
	Klumb and Lückert	
190	0	11020
200	0	10975
210	0	10926
220	0	10874
	Mündel	
210	0	10874
220	0	10887
	API Tables	
260	2 ^a , 2 ^b	10903
280	4, 5	10896
300	9, 9	10892
320	15, 16	10890
340	26, 28	10887
360	40, 42	10882
380 ^c	59, 63	10878

^aThis column based on equation of state of Weltner and Pitzer.

^bThis column based on equation of state of Kretschmer and Wiebe.

^cThe vapor pressure at this temperature is 4.324 atm.

Correction for thermal transpiration between sample and gage was made with an approximate form of the Weber equation (15) using the parameters, $d = 3$ mm., and $\gamma = 173P_2$.

Reagent grade anhydrous methanol was used. The sample was placed in the vacuum system over calcium hydride to remove the last traces of water and then distilled directly into the measuring system. The measured vapor pressures were:

T, ° K.	P(Microns)
175.04	1.27
175.58	1.37
176.46	1.51
177.12	1.80
178.11	2.05
179.05	2.43
180.25	3.08

CALCULATIONS

The heat of sublimation at absolute zero, $\Delta H_{\text{sub}}^{\circ}$, was calculated from the vapor pressure with the relation:

$$-RT \ln P - RT \ln f/P = \Delta(G^{\circ} - H_{\text{sub}}^{\circ}) + \Delta H_{\text{sub}}^{\circ} \quad (1)$$

Independent values of $\Delta H_{\text{sub}}^{\circ}$ (hereafter marked with a prime) were obtained from calorimetric values of the heat of vaporization through the relation:

$$L + (H^{\circ} - H_p) = \Delta(H^{\circ} - H_{\text{sub}}^{\circ}) + \Delta H_{\text{sub}}^{\circ} \quad (2)$$

$$(H^{\circ} - H_p) = \int_0^P \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right] dP$$

Finally, comparison of the spectroscopic and calorimetric entropies was made with the relation:

$$S^{\circ}(\text{spec.}) - S^{\circ}(\text{calor.}) = \frac{\Delta H_{\text{sub}}^{\circ} - \Delta H_{\text{sub}}^{\circ}'}{T}$$

Values of the thermodynamic functions of the ideal gas were taken from a previous tabulation (8). These values fell nicely between those based on the two latest vibrational assignments (3, 12). Thus, at 380° K., the two latest assignments yielded the values, $(H^{\circ} - H_{\text{sub}}^{\circ}) = 3639$ and 3653 cal./mole, respectively, whereas the value used here was 3644. The corresponding spread for $(G^{\circ} - H_{\text{sub}}^{\circ})$ was only 4 cal./mole at 380° K. To obtain values of the thermodynamic functions of the liquid above 320° K., it was necessary to extrapolate the heat capacity data (2) with the aid of earlier measurements (4, 5). Some extrapolated values of the heat capacity in cal./mole ° C. were: 340° K., 21.96; 360° K., 23.49; and 380° K., 25.15. Values of L were taken from the extensive calorimetric determinations between 0° and 130° C. (4).

The vapor pressure above 260° K. was calculated from the Antoine equation (1), $\log P(\text{mm. of Hg}) = 8.07246 - 1574.99/(T - 34.29)$. Two sets of vapor pressure data in the moderately low pressure range have been reported (9, 16). These were included in the calculations involving Equation 1, which have been summarized in Table I. A rapid change in $\Delta H_{\text{sub}}^{\circ}$ with respect to temperature indicated that one of the sets (9) was probably in error. The vapor pressure data presented in this paper led to an average value, $\Delta H_{\text{sub}}^{\circ} = 10904 \pm 8$ cal./mole. A slight drift in $\Delta H_{\text{sub}}^{\circ}$ was discernible at temperatures where the real gas correction term was significant.

Calculations with Equation 2 (Table II), in which the real gas term, $H^{\circ} - H_p$, was quite large, yielded a clear temperature dependence in $\Delta H_{\text{sub}}^{\circ}$ with the result that the entropy test (Table III) depended rather strongly on the choice of temperature. It seems likely that the equation of state of the vapor is the weakest link here, since the

Table II. Heat of Sublimation of Methanol at Absolute Zero Based on Calorimetric Heats of Vaporization

T, ° K.	Cal./Mole			
	H° - H _p		ΔH ₈ '	
280	78 ^a	58 ^b	10859 ^a	10839 ^b
300	146,	111	10896,	10861
320	219,	188	10911,	10880
340	322,	306	10932,	10916
360	407,	423	10911,	10927
380	527,	578	10901,	10952

^aThis column based on equation of state of Weltner and Pitzer.

^bThis column based on equation of state of Kretschmer and Wiebe.

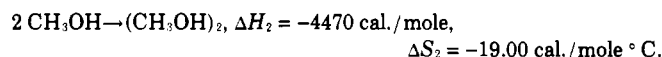
Table III. Comparison of Spectroscopic and Calorimetric Entropies of Ideal Gaseous Methanol

T, ° K.	S°(spec.) - S°(calor.), Cal./Mole ° C.	
280	0.13 ^a	0.20 ^b
300	-0.01,	0.10
320	-0.07,	0.03
340	-0.13,	-0.09
360	-0.08,	-0.13
380	-0.06,	-0.19

^{a,b} See footnotes to Tables I, II.

error in the real gas term can be sharply dependent on temperature in a manner difficult to predict, while errors in the entropies of the liquid and ideal vapor will cumulate slowly with increasing temperature. Thus, although it might be anticipated that the entropy check should be best at 280° K., the lowest temperature of comparison, since the real gas term is smallest, the equation of state is least reliable at this temperature, being based as it is on data at higher temperatures.

Using the dimer-tetramer model for the vapor (10, 19) it was possible to improve the third law calculations by choosing the following constants:



This is shown in Table IV. The specific equations employed were:

$$-RT \ln f/P = -RTe^{\Delta S_2/R} e^{-\Delta H_2/RT} P - RTe^{\Delta S_4/R} e^{-\Delta H_4/RT} P^3$$

$$H^\circ - H_p = -\Delta H_2 e^{\Delta S_2/R} e^{-\Delta H_2/RT} P - \Delta H_4 e^{\Delta S_4/R} e^{-\Delta H_4/RT} P^3$$

Not included here is the small, positive, temperature independent part of the second virial coefficient, which is stated to be about 90 cc./mole (10, 19), and which would contribute -9 cal./mole to each of the real gas terms at 380° K., -5 cal./mole at 360° K., and a negligible amount at lower temperature. It is probably too severe a burden on the rest of the data used in the third law calculations

Table IV. Heat of Sublimation of Methanol at Absolute Zero Recalculated with Adjusted Equation of State

T, ° K.	Cal./Mole			
	-RT ln f/P	ΔH ₈	H° - H _p	ΔH ₈ '
260	3	10904
280	7	10899	124	10905
300	14	10897	155	10905
320	24	10899	208	10900
340	40	10900	294	10904
360	59	10900	390	10894
380	87	10904	523	10897

to expect that this adjusted equation of state is accurate. Rather, an improved equation of state for methanol vapor must come from more direct methods.

NOMENCLATURE

- f = fugacity of vapor at saturation pressure
 G = molar Gibbs free energy
 H = molar enthalpy
 L = molar heat of vaporization
 P = vapor pressure
 R = gas constant, 1.98726 cal./mole ° K.
 S = molar entropy
 T = absolute temperature
 V = molar volume of vapor

LITERATURE CITED

- Am. Petrol. Inst. Research Proj. 44, *Natl. Bur. Standards* (U. S.), Selected Values of Properties of Hydrocarbons.
- Carlson, H.G., *U. S. At. Energy Comm. TID-15153* (1962).
- Falk, M., Whalley, E., *J. Chem. Phys.* **34**, 1554 (1961).
- Fiock, E.F., Ginnings, D.C., Holton, W.B., *J. Research Natl. Bur. Stds. (U. S.)* **6**, 881 (1931).
- Hough, E.W., Mason, D.M., Sage, B.H., *J. Am. Chem. Soc.* **72**, 5775 (1950).
- Ishii, H., Nakayama, K., *Trans. Eighth Natl. Vacuum Symp. (AVS)* **1**, 519 (1961).
- Ivash, E.V., Dennison, D.M., *J. Chem. Phys.* **21**, 1804 (1953).
- Ivash, E.V., Li, J.C.M., Pitzer, K.S., *Ibid.* **23**, 1814 (1955).
- Klumb, H., Lückert, J., *Vakuum-Tech.* **8**, 62 (1959).
- Kretschmer, C.B., Wiebe, R., *J. Am. Chem. Soc.* **76**, 2579 (1954).
- Krishna Murti, G.S.R., *Indian J. Phys.* **33**, 458 (1959).
- Margottin-Maclou, M., *J. phys. radium* **21**, 634 (1960).
- Miller, G.A., *J. CHEM. ENG. DATA* **7**, 353 (1962).
- Miller, G.A., *Ibid.* **8**, 69 (1963).
- Miller, G.A., *J. Phys. Chem.* **67**, 1359 (1963).
- Mündel, C.F., *Z. phys. Chem.* **85**, 435 (1913).
- Podgurski, H.H., Davis, F.N., *J. Phys. Chem.* **65**, 1343 (1961).
- Tauer, K.J., Lipscomb, W.N., *Acta Cryst.* **5**, 606 (1952).
- Weltner, W., Jr., Pitzer, K.S., *J. Am. Chem. Soc.* **73**, 2606 (1951).
- Zerbi, G., Overend, J., Crawford, B., *J. Chem. Phys.* **38**, 122 (1963).

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