[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF CALIFORNIA]

Methyl Alcohol: The Entropy, Heat Capacity and Polymerization Equilibria in the Vapor, and Potential Barrier to Internal Rotation

BY WILLIAM WELTNER, JR., AND KENNETH S. PITZER

The heat capacity of gaseous methanol was measured in a flow calorimeter over the range 345 to 521°K. at pressures of roughly $^1/_3$, $^2/_3$ and 1 atm. The results at 345° K. show a very large and distinctly non-linear trend with pressure. This is interpreted as indicating the presence of methanol tetramers in the gas, somewhat analogous to the polymers of hydrogen fluoride. The heat of dissociation of this tetramer is found to be 24,200 cal./mole which corresponds to a hydrogen bond energy of 6050 cal./mole if the tetramer is a ring. Experimental values from the literature and from this research for the heat capacity and entropy of methanol are compared with values calculated from spectroscopic data, including particularly a potential barrier to internal rotation of 932 cal./mole. Agreement is obtained, but there remain uncertain elements in the spectroscopic data which could affect this result. The apparent variance of this conclusion from that of earlier investigators is due to the unsuspected type of gas imperfection. In addition values are reported for the heat capacity of benzene vapor at several temperatures and for the heat of vaporization of benzene and methyl alcohol.

The potential barrier to internal rotation in methyl alcohol has been the subject of a long series of investigations.[1] The infrared spectrum was first interpreted by Koehler and Dennison[2] to indicate a barrier of about 450 cm.$^{-1}$ (1300 cal./mole). The microwave spectrum, together with further infrared measurements, have been found by Burkhard and Dennison[3] to indicate a barrier of 326 cm.$^{-1}$ (932 cal./mole) which was used by Halford[1] in calculations. However, the experimental value of the entropy has appeared to be inconsistent with as low a barrier as this unless a considerable residual entropy at 0°K. were assumed. Values of the heat capacity of the ideal gas obtained by Eucken and Franck[4] and by Rowlinson[5] were less definitely inconsistent with the spectroscopic barrier but also indicated higher values. Furthermore, the gas heat capacity measurements at 1 atm. of DeVries and Collins[6] show a most unusual increase with decreasing temperature near the saturation curve.

In the present paper measurements are reported of the heat capacity of gaseous methanol at a series of pressures and temperatures. The pressure dependence near the saturation curve indicates a polymerization phenomenon somewhat similar to that observed in hydrogen fluoride. This special type of gas imperfection requires revision of earlier calculations[1] which were based on more conventional behavior.

Experimental

Gaseous Flow Calorimeter.—The calorimeter and its appendages were newly constructed and followed closely the design of Waddington, Todd and Huffman,[7] reference also being made to the apparatus of Pitzer[8] and that of Coleman and DeVries.[9] There were several significant differences which are described in detail elsewhere.[10] These differences will be only briefly mentioned here.

A magnetically actuated valve, constructed from spherical ground glass joints, was employed to divert the vapor stream for a timed interval into a collection vessel. Also it was arranged so that the flow continued as vapor through the heated valve system to the collection vessel which contained the condensing surfaces cooled with ice. The electrical circuit was such that the relay which actuated the magnetic valve also actuated a stop clock for timing the sample takeoff time.

A floating heater was employed in the vaporizer. This consisted of a thin glass float and chromel wire heater arranged to slide vertically on tungsten wire guides which served also as electrical lead wires. Also in the tube returning liquid to the vaporizer an appropriate side tube allowed the liquid to flash off superheat or entrained vapor bubbles.

The platinum resistance thermometers were initially calibrated in the usual way at the ice, steam and sulfur points. After assembly into the flow calorimeter unit they were compared with N.B.S. calibrated mercury thermometers. This second calibration indicated small but significant changes and was adopted for our calculations.

Measurement Procedure.—The procedure for measurement of heat capacities was, for the most part, that described by Waddington, Todd and Huffman.[7] However, many of the heat capacity runs were made simultaneously with heat of vaporization determinations so that any error due to incorrect flow rate measurements was eliminated here. Upon applying the corrections of Waddington, *et al.*, to the heats of vaporization, agreement within ±0.1% was obtained between heat capacities measured simultaneously with heats of vaporization and those measured in the usual way.

The heats of vaporization were measured by collecting 20 to 40 ml. of liquid in the trap cooled by ice-water over a period of 1.5 to 8 minutes depending upon the rate of flow which varied from 0.05 to 0.16 mole/min. Readings of the power supplied to the vaporizer and the resistances of the thermometers were made during the collection period; at slow flows, readings were made every minute; at fast flows, as rapidly as possible. A correction for change in the depth of immersion of the vaporizer heater during the measurement was unnecessary since a floating heater was employed. Also, the variation in boiling temperature was small enough to be neglected. However, the corrections for heat dissipated in the tungsten leads of the vaporizer and for increasing vapor volume, due to decreasing liquid volume in the vaporizer, amounted to about 1% of the heat of vaporization and were therefore quite significant.

The estimated limits of error are given along with the results at various points. The average deviation was usually much less and was about 5 cal./mole for heats of vaporization. The precision of the heat capacity measurements was in general quite good except for methanol at 72.4°. Divergence from a straight line amounted to about 0.02 cal./mole deg. when the apparent measured heat capacities were plotted *versus* the reciprocal of the rate of flow. At infinite rate of flow ($1/F = 0$) the heat capacities as determined by thermometers T_2 and T_3 agreed within 0.03 cal./mole deg. except for those measured for methanol at 72.4° and 755 and 500 mm. where the discrepancy was about 0.1 cal./mole deg.

Materials.—C.P. thiophene-free benzene was distilled from freshly cut sodium through an all-glass column, having 30 perforated plates. Only the middle cut was used.

Commercial absolute, acetone-free methanol was dried

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[1] J. O. Halford, *J. Chem. Phys.*, **18**, 361, 1051 (1950), reviews the situation and gives earlier references.

[2] J. S. Koehler and D. M. Dennison, *Phys. Rev.*, **57**, 1006 (1940).

[3] Private communication from Professor D. M. Dennison.

[4] A. Eucken and E. U. Franck, *Z. Elektrochem.*, **52**, 195 (1948).

[5] J. S. Rowlinson, *Nature*, **162**, 820 (1948).

[6] T. DeVries and B. T. Collins, THIS JOURNAL, **63**, 1343 (1941).

[7] G. Waddington, S. S. Todd and H. M. Huffman, *ibid.*, **69**, 22 (1947).

[8] K. S. Pitzer, *ibid.*, **63**, 2413 (1941).

[9] C. F. Coleman and T. DeVries, *ibid.*, **71**, 2839 (1949).

[10] Ph.D. Dissertation of William Weltner, Jr., University of California, 1950.

with sodium by the method of Gillo[11] and distilled through the same all-glass column with a continuous flow of dry nitrogen bubbling through the methanol and up the column. It was stored in the dark in a vessel closed by stopcocks greased with Apiezon M. This grease was found to be quite insoluble in methanol.

Results with Benzene.—Measurements were made on benzene to check the operation of the new calorimeter. Table I gives the heat capacities of benzene measured at 1 atm. pressure as compared with those of Scott, Waddington, Smith and Huffman.[12]

TABLE I

HEAT CAPACITY (CAL./MOLE DEG.) OF BENZENE AT 1 ATM. PRESSURE

T, °K.	This research	Scott, *et al.*	Difference
375.0	25.99	25.84	+0.15
403.0	27.60	27.52	+ .08
463.0	30.90	31.24	− .34

The results of Scott, *et al.*, were plotted to obtain the values corresponding to the temperatures of measurement in this research. The differences in Table I seem too large to be accounted for by expected magnitudes of error but are not excessive in comparison with most measurements of gaseous heat capacities.

The heat of vaporization of benzene at 1 atm. pressure was determined to be 7358 ± 15 cal./mole as an average of seven measurements made over the range of flow rates. This compares excellently with the values of Scott, *et al.*,[12] and Fiock, Ginnings and Holton,[13] which are 7349 and 7353 cal./mole, respectively.

Results with Methanol.—The heat capacities were measured at four temperatures from 345 to 521°K. and at 755, 500 and 260 mm. pressure at each temperature. The values obtained are given in Table II together with the estimated accuracy which is the same for the three pressures at a given temperature. The values in Table II for the ideal gas were obtained from those at 260 mm. by use of the gas imperfection equations to be described below. The values in Table II are shown in Fig. 1 along with the values of DeVries and Collins.[6] The curves in Fig. 1 are theoretical and will be discussed later but it is apparent that our results at 755 mm. are quite consistent with those of DeVries and Collins.

TABLE II

HEAT CAPACITY (CAL./MOLE DEG.) OF METHYL ALCOHOL

T, °K.	Pressure (mm.)			Est. uncertainty	Ideal gas
	755	500	260		
345.6	21.03	14.72	12.18	±0.2	11.46 ± 0.3
403.2	12.96	12.75	12.58	± .05	12.43 ± .1
464.0	13.94	13.84	13.74	± .1	13.67 ± .1
521.2	14.68	14.62	14.48	± .2	14.44 ± .3

The heats of vaporization obtained for methanol to saturated vapor at 755, 500 and 260 mm. pressure are given in Table III along with the values of Fiock, Ginnings and Holton.[13] Except for that at 260 mm., the values given are an average of at least four measured heats of vaporization over the range of flow rates. The measured heats of vaporization at 260 mm. pressure showed a marked decrease with increase in the rate of flow of vapor. The value given in Table III corresponds to the intercept at $1/F = 0$ when the heat of vaporization is plotted against the reciprocal of the rate of flow. The heats of vaporization measured in this research agree with those of Fioch, *et al.*, well within the estimated uncertainties.

TABLE III

HEATS OF VAPORIZATION (CAL./MOLE) OF METHANOL TO SATURATED VAPOR

T, °K.	P (mm.)	This research	Fiock, *et al.*,
337.8	755	8442 ± 15	8429
327.9	500	8579 ± 15	8576
313.1	260	8768 ± 25	8774

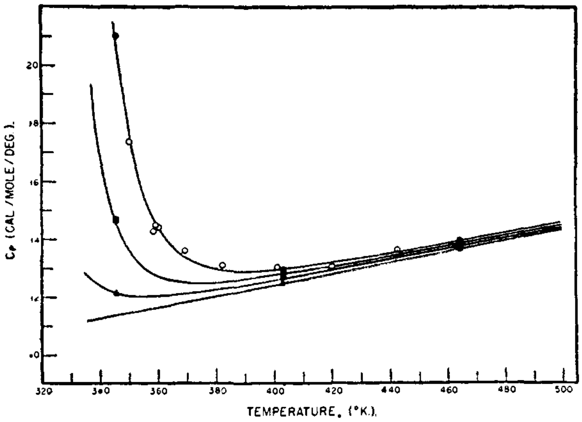

Fig. 1.—Heat capacity of methanol vapor at 755, 500, 260 mm. and in the ideal gas state: ○, experimental values of DeVries and Collins at 750 mm.; ●, experimental values of this research at 755 mm.; ■, at 500 mm.; ▲, at 260 mm. Solid lines indicate calculated values at 755, 500, 260 mm. and in the ideal gas state using Stepanov's vibrational assigument and the gas imperfection equations of this research.

Calculations and Discussion

Gas Imperfection.—From Table II or Fig. 1 it is apparent that at 345°K. the trend of heat capacity with pressure is far from linear. Considering that all the data are for pressures below one atmosphere, this is very unusual and is suggestive of the behavior of hydrogen fluoride in forming polymers in the gas. The formation of reasonably strong hydrogen bonds is the point of similarity between hydrogen fluoride and methanol which is undoubtedly the cause of these polymerizations.

However, by 464°K. the curve of C_p *vs.* P is quite clearly linear, showing that the second virial coefficient (which corresponds to dimerization) is here the only significant form of gas imperfection. The data on $P-V-T$ measurements for methanol are relatively few. Eucken and Meyer[14] made measurements from 352 to 374°K. at a single gas concentration. The old work of Ramsay and Young[15] covers a wide range but is not accurate enough to serve as more than a general check in the low pressure, low temperature region.

Since we have few data, it was essential to select a representation of the complex behavior containing a minimum of disposable constants. The system selected contains five: the heat and entropy of formation of the gaseous dimer, the number of monomer units in the higher polymer and the heat and entropy of formation of the higher polymer. A value (the same as Eucken and Meyer's) was assumed for the covolume, which is unimportant at these temperatures and pressures anyway.

Several authors[12,16] have recently used the form of equation for the second virial coefficient which

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(11) L. Gillo, *Ann. chim.*, **12**, 281 (1939).

(12) D. W. Scott, G. Waddington, J. C. Smith and H. M. Huffman, *J. Chem. Phys.*, **15**, 565 (1947).

(13) E. F. Fiock, D. C. Ginnings and W. B. Holton, *J. Research Natl. Bur. Standards*, **6**, 881 (1931).

(14) A. Eucken and L. Meyer, *Z. physik. Chem.*, **5B**, 452 (1929).

(15) W. Ramsay and S. Young, *Roy. Soc. London, Phil. Trans.*, **A178**, 313 (1887).

(16) J. O. Hirshfelder, F. T. McClure and I. F. Weeks, *J. Chem. Phys.*, **10**, 201 (1942).

corresponds to a constant energy of dimerization, *i.e.*, ΔC of dimerization is zero. This is given by a square well potential model. If the walls of the potential well are sloped, or if the rotation of the component monomer units is restricted in the polymer, the relative heat capacity of the polymer will be increased as compared to the square model (and a given monomer). Thus it seemed to us to be a better (though still arbitrary) assumption to make the heat of polymerization (or dimerization) constant and ΔC_p of polymerization zero. The equations yielded by this model in the virial coefficient form (appropriate for small fractions of polymer) are

$$PV = RT + BP + DP^{n-1} \quad (1)$$

$$B = b - RT/K_2 = b - RTe^{-\Delta S_2/R}e^{\Delta H_2/RT} \quad (2)$$

$$D = -(n - 1)RT/K_n = -(n - 1)RTe^{-\Delta S_n/R}e^{\Delta H_n/RT} \quad (3)$$

where b is the covolume, n is the number of monomer units in the higher polymer, K_2 and K_n are pressure equilibrium constants of dissociation for dimer and higher polymer, respectively. The corresponding expressions for the heat capacity are

$$C_p = C_p^0 + aP + cP^{n-1} \quad (4)$$

$$a = \frac{\Delta H_2^2}{RT^2}e^{-\Delta S_2/R}e^{\Delta H_2/RT} \quad (5)$$

$$c = \frac{\Delta H_n^2}{RT^2}e^{-\Delta S_n/R}e^{\Delta H_n/RT} \quad (6)$$

The heat capacity data at 345.6°K. were clearly fitted better by $n = 4$ than any other integral value, consequently the higher polymer was assumed to be a tetramer. The following successive approximation method was employed to evaluate the other constants. ΔH_2 and ΔS_2 were obtained from the Eucken and Meyer *P–V–T* data assuming only dimerization and the resulting value of a in equations (4) and (5) calculated. The values of C_p at about one atmosphere from 340 to 390°K. (both DeVries and Collins measurements and those of this research) were then used[17] to evaluate ΔH_4 and ΔS_4. Then ΔH_2 and ΔS_2 were recalculated recognizing the presence of tetramer and the cycle repeated until no significant changes occurred on further repetition. The resulting equations for the second and fourth virial coefficients are

$$B = 80 - 0.0206Te^{3220/RT}\ \text{cc./mole} \quad (7)$$

$$D = -4.36 \times 10^{-16}\ Te^{24200/RT}\ \text{cc./mole atm.}^2 \quad (8)$$

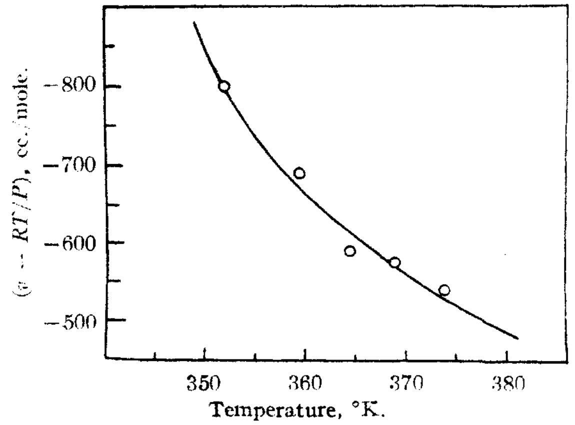


Fig. 2.—(v − RT/P) of methanol vapor as a function of temperature. Circles are experimental results of Eucken and Meyer. Solid line indicates results calculated from equation of state found in this research.

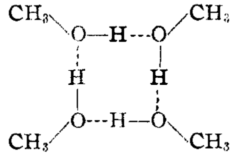
The thermodynamic constants at standard states corresponding to these virial coefficients are

$\Delta H_2 = 3220$ cal./mole $\quad \Delta S_2 = 16.5$ cal./deg. mole

$\Delta H_4 = 24200$ cal./mole $\quad \Delta S_4 = 81.3$ cal./deg. mole

The agreement of our calculated values of $v - RT/P$ with Eucken and Meyer's measurements is shown in Fig. 2. Our calculated *P–V–T* behavior has also been checked with the data of Ramsay and Young and yields agreement within experimental error in the range of temperature of interest here, *i. e.*, up to about 400°K.

It is interesting to note that the heat of dissociation of the tetramer, 24,200 cal./mole, corresponds to a hydrogen bond energy of 6,050 cal. if the tetramer is a ring molecule.



Actually our data do not distinguish between the formation of tetramers and the formation of an appropriate mixture of trimer, tetramer, pentamer, etc. Thus it is difficult to estimate the reliability of this value of the hydrogen bond energy.

Our value of 6.05 kcal./mole for the hydrogen bond energy in the gaseous polymer is very close to the value 6.2 kcal./mole estimated by Pauling[18] from the heat of sublimation of methanol.

For hydrogen fluoride, Long, Hildebrand and Morrell[19] found a heat of dissociation of about 41,000 cal./mole for a hexamer corresponding to a hydrogen bond energy of 6800 cal.

The essential conditions for the formation of polymers of this type would appear to be as follows: (1) The principal intermolecular attraction is hydrogen bonding. (2) There is only one hydrogen available per molecule. (3) The geometry is such that a dimer with two hydrogen bonds is not possible. Failure of condition (3) leads to principally dimeric vapor as in the simpler carboxylic acids while the failure of either (1) or (2) makes the liquid with its larger effective coördination number so stable that the ring type polymers cannot be detected.

Gas Heat Capacity.—Halford[1] has calculated the contribution to various thermodynamic functions from internal rotation based on the 932 cal./mole potential barrier and 1.01 × 10^{-40} g. cm.^{2} moment of inertia for the OH group found by Burkhard and Dennison.[3] Halford's values for the other moments of inertia appear to be sound but the

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[17] It was necessary to assume a curve for the ideal gas heat capacity at this point. However, the gas imperfection effect is so large that the result is not sensitive to the exact curve assumed.

[18] L. Pauling, "The Nature of the Chemical Bond," second edition, Cornell University Press, Ithaca, N. Y., 1945, p. 304.

[19] R. W. Long, J. H. Hildebrand and W. E. Morrell, This Journal, 65, 182 (1943).

vibration frequency assignment still has its doubtful aspects. Halford states, "Noether's assignment has been used in the present (Halford's) calculations, merely because it is the later one, although it is not obvious that it is the correct one." After a careful review of the situation we believe Noether[20] and Stepanov[21] are probably correct with respect to the nine frequencies which they assign in essentially the same way. They differ as to the two methyl rocking motions and we do not believe the present spectroscopic data are adequate to justify a firm choice. However, the difference is not large, for thermodynamic calculations, Noether's values being 1250 and 1209 cm.$^{-1}$ while Stepanov's are 1034 and 1104 cm.$^{-1}$. In our calculations we have obtained values for each of these vibrational assignments.

In Fig. 3 are shown the various experimental values for the heat capacity of gaseous methanol reduced to the ideal gas. DeVries and Collins values were reduced by the use of our equations for gas imperfection given above. It is apparent that agreement is obtained within the range of uncertainty in vibrational assignment. However, Professor Dennison[3] informs us that the final spectroscopic values for the potential barrier and moments of inertia, although in the vicinity of those used in these calculations, will probably differ significantly therefrom. Thus no conclusion as to the relative merits of the two vibrational assignments should be drawn at this time.

In Fig. 1 are shown the heat capacity data at various pressures as compared with curves calculated from ideal gas values with Stepanov's frequencies and our gas imperfection equations. It is apparent that the agreement is good, confirming in this case principally the assumptions as to polymerization in the gas.

Entropy.—The necessary low temperature heat capacity measurements have been made by Kelley[22] who calculated the entropy of the liquid at 298.16° K. Combining this result with the heat of vaporization data of Fiock, Ginnings and Holton[13] yields the values of the experimental entropy of methanol listed in Table IV covering the range 298.16 to 380° K. The entropy of the ideal gas was calculated by Halford[1] for the 932 cal./mole potential barrier. We have used Stepanov's vibrational assignment at this point because of the somewhat better agreement shown for the gas heat capacity. Our treatment of the gas imperfection given above was employed to convert from the ideal gas to the real gas at the vapor pressure.

$$S^0 - S_p = R \ln P + \frac{dB}{dT}P + \frac{dD}{dT}\cdot\frac{P^3}{3} \qquad (9)$$

where S^0 is standard entropy of ideal gas at 1 atm. and S_p is the entropy of the real gas at pressure P.

The last two columns in Table IV show agreement between calculated and experimental entropies well within the estimated error of about 0.3 cal./deg. mole. Actually, the use of Noether's vibration frequencies would have given even more perfect agreement. Again the preliminary nature of the spectroscopic potential barrier and moments of inertia makes detailed conclusions premature. Nevertheless, there is no evidence for a significant residual entropy in the crystals at 0°K.

TABLE IV

ENTROPY OF METHYL ALCOHOL

Units of entropy; cal./deg. mole; P = vapor pressure

T, °K.	S^0, calcd. ideal gas	$R \ln P$	$\frac{dB}{dT}P$	$\frac{dD}{dT}\cdot\frac{P^3}{3}$	S_p calcd.	S_p exptl.
298.16	57.21	−3.60	0.08	0.31	60.42	60.28
320	57.97	−1.51	.15	.44	58.89	58.78
340	58.63	+0.16	.24	.54	57.69	57.63
360	59.29	1.60	.35	.62	56.72	56.64
380	59.92	2.88	.49	.69	55.86	55.74

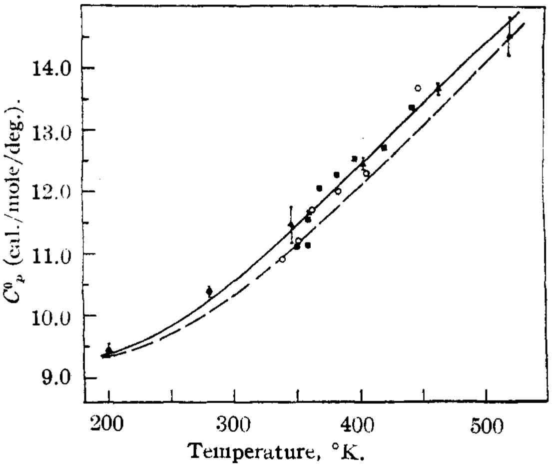

Fig. 3.—Heat capacity of methanol vapor in the ideal gas state: ●, experimental results of Eucken and Franck; ■, experimental results of DeVries and Collins reduced to the ideal gas by the gas imperfection equations of this research; O, experimental results of Rowlinson; ▲, results of this research from Table II. Vertical lines through points indicate estimated limits of error: —, calculated heat capacities using Stepanov's vibrational assignment; — — —, using Noether's vibrational assignment.

From Table IV one may also note that the corrections for gas imperfection (sum of items in columns 4 and 5) are unusually large. For the vapors of normal liquids the entropy correction is usually between 0.1 and 0.2 cal./deg. mole at the boiling point and it decreases rapidly at lower temperatures. In view of this situation it is not surprising that earlier attempts to fit the calculated and experimental entropies led to failure (or to excessively high calculated barriers to internal rotation). Even the gas imperfection corrections based on Eucken and Meyer's second virial coefficient as calculated by Halford are about 0.3 cal./deg. mole lower than we find.

Conclusions.—By taking proper account of the unexpected gas phase polymerization of methyl alcohol vapor, it has been possible to bring the various experimental thermodynamic quantities into agreement with values calculated from the tentative spectroscopic barrier (932 cal./mole) to internal rotation and vibration frequency assignment. Measurements of the heat capacity of a gas at different pressures are a powerful tool in

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[20] H. D. Noether, *J. Chem. Phys.*, **10**, 693 (1942).

[21] B. E. Stepanov, *J. Phys. Chem.* (*U. S. S. R.*), **19**, 497 (1945).

[22] K. K. Kelley, THIS JOURNAL, **51**, 181 (1929).

investigating gas imperfection and were the essential element in the solution of this long baffling problem.

While it has been shown that the thermodynamic data are consistent with these spectroscopic constants, other values of the spectroscopic quantities within certain limits are allowed. It seems hardly worth while to investigate this extensively at present. Nevertheless, even though the principal dilemma concerning the potential barrier and entropy of methanol is now removed, the exact 932 cal./mole value for the barrier is only as certain as the spectroscopic data indicate. Considering the uncertainty in the vibration frequency assignment, the thermodynamic data might be consistent with any barrier within a few hundred calories of this 932 cal. figure. Moreover, if the moment of inertia of the OH group (for torsion) is substantially larger than the 1.01×10^{-40} here assumed, then an appreciably higher barrier would be indicated. This moment of inertia requires either an abnormally large C–O–H angle or an abnormally short O–H distance.

Acknowledgments.—We wish to acknowledge the great assistance of Dr. Gordon M. Barrow in the construction of the calorimeter and in making available to us the second set of thermometer calibrations mentioned above. We also wish to thank Professor W. D. Gwinn for his helpful advice and guidance, particularly while one of us (K. S. Pitzer) was away from Berkeley.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

The Temperature–Interfacial Tension Studies of Some Alkyl Esters of Monobromoacetic Acid against Water[1]

BY JOSEPH J. JASPER AND WILLIAM J. MAYER

This is the second of a series of interfacial tension studies of the methyl, ethyl, *n*-propyl and *n*-butyl esters of the monohalogenated acetic acids against water. The present paper involves the interfacial tension measurements of the above esters of monobromoacetic acid at four temperatures between 26.8 and 70.4° against water, the two liquids being mutually saturated. With the aid of least squares, empirical equations were formulated which relate the interfacial tensions to the temperature. The data are tabulated in density–temperature and interfacial tension–temperature tables. The empirical equations were used to calculate the latent heat and enthalpy of formation per sq. cm. of interfacial surface. These are presented in a table.

Although the interfacial tensions of many organic liquid compounds measured against water have appeared in the literature, such data are generally inadequate since they include no appreciable temperature ranges nor present any correlation with the properties of the molecular species involved. As a consequence, interfacial tension data, of potentially great usefulness in numerous aspects of theoretical and industrial chemistry, are meager or non-existent.

The purpose of this investigation was to obtain interfacial tension data for the lower esters of monobromoacetic acid with water over an appreciable temperature range, and to formulate empirical equations relating these variables. The present study represents the second of a series[2] which will eventually include the corresponding esters of other monohalogen acetic acids, and also other homologous series containing substituted halogen groups.

Experimental

Preparation and Purification of the Ester.—The methyl, ethyl, *n*-propyl and *n*-butyl esters of monobromoacetic acid were used in this study. The methyl and ethyl esters were obtained from the Eastman Kodak Company, while the *n*-propyl and *n*-butyl esters were prepared by us. The method of preparation was that of Fisher as described by Fieser and Fieser.[3] The esters were subjected to vacuum fractionation for their final purification. The apparatus and procedure were exactly the same as previously described for the four alkyl esters of monochloroacetic acid.[2]

Determination of the Densities.—The densities play an important role in the determination of interfacial tension. Since they appear in the equation as explicit variables, they must be determined directly and accurately. A modified form of the "type D" pycnometer described by Weissberger[4] was used. Three pycnometers were constructed as nearly alike as possible in form and dimensions. Two of these were used for the respective mutually saturated liquids and the third as a counterpoise. Repeated trials showed a deviation in the densities no greater than 0.05 per cent. even

TABLE I

DENSITY DATA FOR THE MUTUALLY SATURATED LIQUID COMPOUNDS

Ester	Temp., °C.	Density: Ester saturated with water	Density: Water saturated with ester
Methyl	26.8	1.6408	1.0159
	42.6	1.6135	1.0103
	55.2	1.5902	1.0047
	70.4	1.5628	0.9972
Ethyl	26.8	1.4947	1.0028
	42.6	1.4695	0.9972
	55.2	1.4501	.9918
	70.4	1.4254	.9835
n-Propyl	26.8	1.4024	.9984
	42.6	1.3796	.9929
	55.2	1.3615	.9875
	70.4	1.3394	.9800
n-Butyl	26.8	1.3366	.9974
	42.6	1.3158	.9921
	55.2	1.2994	.9867
	70.4	1.2789	.9787

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[1] Presented before the Division of Physical and Inorganic Chemistry at the Chicago meeting of the American Chemical Society, September 1950.

[2] J. J. Jasper and W. J. Mayer, THIS JOURNAL, **72**, 4767 (1950).

[3] L. F. Fieser and M. Fieser, "Organic Chemistry," D. C. Heath and Company, Boston, Mass., 1944, p. 133.

[4] A. Weissberger, "Physical Methods of Organic Chemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1945, p. 79.