scribes the conductance behavior to 0.2 N or more. These relationships may be expressed as

$$\Lambda\sqrt{\eta_r} = \Lambda_0 - (\alpha + \beta\Lambda_0)\sqrt{C} \qquad (1)$$

$$\Lambda + (\alpha + \beta\Lambda_0)\sqrt{C} = \Lambda_0 + BC\theta_r \qquad (2)$$

Data derived from plots of $\Lambda\sqrt{\eta_r}$ *versus* $\sqrt{C}$ and $\Lambda + (\alpha + \beta\Lambda_0)\sqrt{C}$ *versus* $C\theta_r$ for three salts are presented in Table IV.

TABLE IV

NEGATIVE SLOPES OF PLOTS DERIVED FROM MODIFIED EQUATIONS FOR N-METHYLPROPIONAMIDE SOLUTIONS

Salt	Temp., °C.	Eq. 1	Eq. 2
KBr	30	10.1	6.9
	40	13.4	7.0
	50	16.7	6.6
	60	21.0	4.7
KI	30	9.3	6.7
	40	11.7	5.6
	50	14.2	5.4
	60	17.7	2.7
NaI	30	9.2	5.5
	40	11.6	5.7
	50	14.5	3.2
	60	11.7	2.4

In all cases the Walden product, $\Lambda_0\eta_0$, decreases as the temperature rises, but only from one-third to one-half as rapidly as in water. The Walden product temperature coefficient is smaller for salts in N-methylbutyramide than in N-methylpropionamide; it is smaller for potassium salts than for the corresponding sodium salts in both solvents. The divergences from a strict proportionality between the viscosity temperature coefficient for the solvent and the mobility temperature coefficient for the ions leads to the conclusion that the conductance phenomenon is associated with a sort of short-range viscosity about each ion. The short-range viscosity may include distortion and other effects resulting from interaction between the solvodynamic unit and molecules or molecular groups about it, which may not change with temperature as much as the bulk viscosity of the solvent. Comparison of data for sodium and potassium salts reveals that, in the N-methylamides, thermal agitation has less effect on the short-range viscosity about the ion having the smaller crystallographic radius. The short-range viscosity around the sodium ion does not decrease with rising temperature as rapidly as the bulk viscosity; the mobility of the ion remains more nearly constant and the product decreases. In water the comparative behavior of the sodium and potassium salts is reversed with the product for the potassium salts decreasing more rapidly. It is evident that in the case of an unsolvated or slightly solvated ion (K^+ in N-methylamides) or an ion with a firmly bound sheath of solvent molecules (Na^+ or Li^+ in water) viscosity effects close to the solvodynamic unit respond to temperature changes much like the viscous forces in the body of the solvent. If the ion is partially solvated (K^+ in water) or its interaction with the solvent consists principally of distortion of the solvent structure (Na^+ in N-methylamides) the short-range viscosity exhibits less response to changes in temperature.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING AT THE UNIVERSITY OF TEXAS]

The Thermodynamic Properties of Acetone

BY ROBERT E. PENNINGTON AND KENNETH A. KOBE

RECEIVED JULY 13, 1956

The vapor heat capacity and heat of vaporization of acetone have been determined calorimetrically. These data were used in conjunction with molecular structure and spectroscopic information to evaluate the barriers to internal rotation in the acetone molecule and to compute tables of the thermodynamic functions. Correlation of the effects of gas imperfection in the experimental data provided an equation of state and the parameters of a Stockmayer potential function for the representation of the intermolecular forces acting in acetone vapor.

As part of a program for the study of thermodynamic properties of the industrially important oxygenated hydrocarbons, the vapor heat capacity of acetone has been determined over a range of temperatures and pressures (338 to 439°K. and $^1/_3$ to $^5/_3$ atm.). These data were used in conjunction with molecular structure and spectroscopic information from the literature to evaluate the barriers to internal rotation in the acetone molecule and to compute tables of the thermodynamic functions at selected temperatures from 0 to 1500°K. Also obtained in the experimental studies were heats of vaporization in the temperature range from 300 to 345°K. Information obtained upon evaluating the effects of gas imperfection in the experimental data has been employed to obtain an equation of state and to indicate something of the nature of the intermolecular forces acting in acetone vapor.

Physical Constants and Definitions.—All data reported here are based on the 1954 Atomic Weights,[1] the values of the fundamental physical constants reported by Rossini, *et al.*,[2] and the following definitions: 0°C. = 273.15°K. and 1 cal. = 4.1840 abs. joules. All measurements of temperature were made with platinum resistance thermometers, so that temperatures reported are on the defined International Temperature Scale.

The Material.—The sample studied was "Baker Analyzed Reagent" acetone with assay of 99.7% acetone; water was

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(1) E. Wichers, THIS JOURNAL, **76**, 2033 (1954).

(2) F. D. Rossini, F. T. Gucker, H. L. Johnston, L. Pauling and G. W. Vinal, *ibid.*, **74**, 2699 (1952).

the chief impurity. Prior to use this material was stored for a period of several days over anhydrous calcium sulfate with occasional agitation. The acetone was transferred to receivers for introduction into the experimental apparatus by simple bulb-to-bulb distillations in which the first and last portions of distillate were always discarded. The distilled acetone was never allowed to come in contact with air or water vapor.

Although the equilibrium constant for the cracking of acetone to ketene and methane is favorable in the experimental temperature range,[3] no evidence of this was observed. Measurements of the heat capacity at the lowest experimental temperatures (338°K.) were made at the beginning and end of operations and no change was found in the value obtained.

The Apparatus.—The apparatus employed in the determinations of vapor heat capacities and heats of vaporization is of the same type as described by Waddington,[4] and includes the later modifications discussed by McCullough, *et al.*[5] All temperature and energy observations were made potentiometrically with a White Double Potentiometer. The voltage of the unsaturated type standard cell used with the potentiometer was obtained from several comparisons with other standard cells which were recently certified by the National Bureau of Standards. The standard resistors either were new and supplied with a manufacturer's certificate or were calibrated in terms of the standards maintained by the Department of Physics at this University. The temperature scale of the platinum resistance thermometers in the apparatus was established by numerous comparisons with a platinum resistance thermometer which had just been returned from certification at the National Bureau of Standards.

In the first trial runs of the apparatus both the vapor heat capacity and heat of vaporization of benzene were measured for several conditions of temperature and pressure. All values obtained agree within better than 0.1% with the results reported by Scott, *et al.*[6] The values obtained for the heat of vaporization at 41.6 and 80.1° are 7864 and 7344 cal. mole^{-1}. The values obtained for the vapor heat capacity at 98.1° and pressures of 760 and 194 mm. are 25.62 and 25.18 cal. mole^{-1} deg.$^{-1}$.

The Heat of Vaporization.—Values of the heat of vaporization determined at five temperatures corresponding to vapor pressures of one-third to five-thirds atmosphere are reported in Table I. These data are the average of three or more determinations at each temperature and the intervals given represent the maximum deviation from the mean. The accuracy uncertainty of the values reported is estimated as not greater than 0.1%. An empirical equation useful for interpolation in these results and for slight extrapolations is

$$\Delta H_v = 938.7(508.7 - T)^{0.386}, \text{ cal. mole}^{-1} \qquad (1)$$

where T is in degrees Kelvin.[7] This equation represents the results given in Table I within the ascribed accuracy uncertainty.

Several earlier investigators have measured the heat of vaporization of acetone at its normal boiling point. The value obtained in this research is 6952 cal. mole^{-1}, which may be compared with 7091 cal. mole^{-1} reported by Matthews,[8] 7164 cal. mole^{-1} reported by Bennewitz and Rossner,[9] and 6940 cal. mole^{-1} reported by Collins, Coleman and DeVries.[10]

TABLE I

THE MOLAL HEAT OF VAPORIZATION OF ACETONE IN CAL.

T, °K.	P, atm.	ΔH_v
300.42	1/3	7372 ± 2
317.90	2/3	7129 ± 1
329.28	1	6952 ± 1
337.94	4/3	6830 ± 2
345.03	5/3	6717 ± 1

The Vapor Heat Capacity.—The vapor heat capacity was studied as a function of pressure at four temperatures. The range of experimental observations included pressures from one-third to five-thirds atmosphere and extended from 338 to 439°K. The results obtained are presented in Table II. The accuracy uncertainty of these data is estimated as being not greater that 0.2%.

TABLE II

THE MOLAL HEAT CAPACITY OF ACETONE VAPOR IN CAL. DEG.$^{-1}$

T, °K.	338.2	371.2	405.2	439.2
C_p (5/3 atm.)		22.67	23.22	24.16
C_p (4/3 atm.)		22.27		
C_p (1 atm.)	21.57	21.89	22.81	23.92
C_p (2/3 atm.)	20.83	21.52		
C_p (1/3 atm.)	20.13	21.17	22.39	23.69
$C_p°$	19.48	20.84	22.21	23.58
$-TB''$ (obsd.)[a]	1.90	0.97	0.56	0.33
$-TB''$ (calcd.)[a]	1.90	1.03	0.61	0.39

[a] $-TB''$ represents the limiting value of $(\partial C_p/\partial p)_T$ at zero pressure. The units are cal. deg.$^{-1}$ mole^{-1} atm.$^{-1}$.

Collins, Coleman and DeVries[10] have measured the vapor heat capacity of acetone at one atmosphere pressure in the temperature range from 333 to 423°K. with an estimated accuracy uncertainty of one to two per cent. In Fig. 1 their results are compared with the values obtained at one atmosphere in this research. Also included in Fig. 1 is the single datum of Bennewitz and Rossner[9] at 410°K.

Correlation of the Effects of Gas Imperfection

Although the polar nature of the acetone molecule gives rise to an unusually large gas imperfection, this can be represented adequately in the range of experimental observations by the use of a second virial coefficient only. However, a volume implicit relation is definitely required to account for the slight curvature observed in plots of heat capacity as a function of pressure. Thus, the equation of state employed is

$$PV/RT = 1 + B/V \qquad (2)$$

A similar situation has been observed in the case of the also highly polar compound nitromethane.[5] In terms of the association concept for accounting for gas imperfections, it appears that the strong dipole interactions in these vapors cause an unusually great number of "dimers" to be present. These "dimers," however, which are comparatively neutral molecules, do not exhibit any greatly enhanced tendencies toward further association. This

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(3) K. A. Kobe and R. H. Harrison, *Petroleum Refiner*, **33**, No. 8, 109 (1954).

(4) (a) G. Waddington, S. S. Todd and H. M. Huffman, THIS JOURNAL, **69**, 22 (1947); (b) G. Waddington and D. R. Douslin, *ibid.*, **69**, 2275 (1947).

(5) J. P. McCullough, D. W. Scott, R. E. Pennington, I. A. Hossenlopp and G. Waddington, *ibid.*, **76**, 4791 (1954).

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

(7) The selected value of the critical temperature, 508.7°K., reported by K. A. Kobe and R. E. Lynn, Jr., *Chem. Revs.*, **52**, 117 (1953), was used as one of the constants in eq. 1.

(8) J. H. Matthews, THIS JOURNAL, **48**, 562 (1926).

(9) K. Bennewitz and W. Rossner, *Z. physik Chem.*, **B39**, 126 (1938).

(10) B. T. Collins, C. F. Coleman and T. DeVries, THIS JOURNAL, **71**, 2929 (1949).

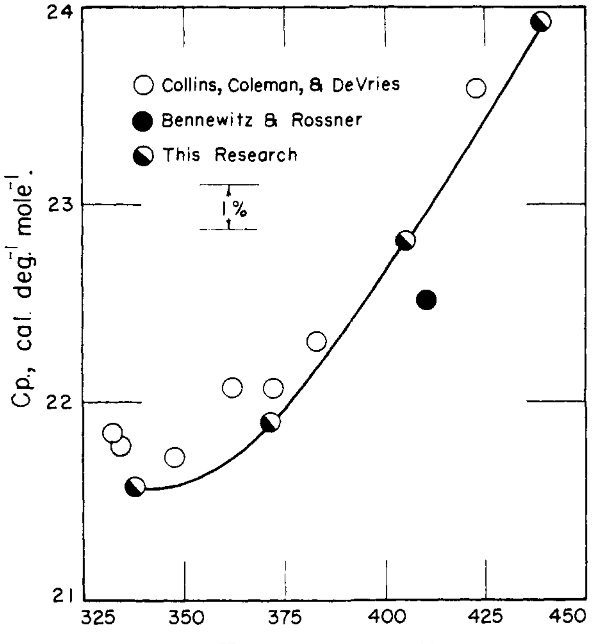

Fig. 1.—The molal heat capacity of acetone vapor at one atmosphere pressure.

is in strong contrast to cases of hydrogen-bonding, occurring for water[11] and the lower aliphatic alcohols,[12] where third and even fourth virial coefficients are required for satisfactory representation in temperature and pressure ranges corresponding to those covered here.

The Heat Capacity in the Ideal Gas State.—Making use of eq. 2 the heat capacity may be represented by

$$C_p = C_p{}^\circ - TB''P + R(T/V)^2[BB'' + V(B' - B/T)^2/(V + 2B)] \quad (3)$$

where the primes indicate differentiation with respect to T, and where the last term on the right, non-linear in pressure, is small in comparison with the others. The values of $C_p{}^\circ$ and $-TB''$ (the limiting value of $(\partial Cp/\partial P)_T$ at zero pressure) reported in Table II were obtained by an iterative procedure. Crude values of the non-linear term in equation 3 were estimated and subtracted from the observed heat capacities. This yielded a linear function of pressure at each temperature with intercept and slope of the corresponding $C_p{}^\circ$ and $-TB''$, respectively. Subsequent refinement in the calculated values of the small non-linear terms provided the final results for $C_p{}^\circ$ and $-TB''$ reported in Table II. Thus, the actual nature of the function adopted for representation of the second virial coefficient enters in only a minor way into the evaluation of the data reported for the heat capacity in the ideal gas state, and any function providing reasonably accurate representation would achieve the same result. The curves drawn in Fig. 2 were obtained by combining the calculated values of the non-linear terms with the *observed* values of $-TB''$ given in Table II. Figure 2 demonstrates the adequacy of use of only a second virial coefficient in representing the effects of gas imperfection on the vapor heat capacity in the experimental range of temperatures and pressures.

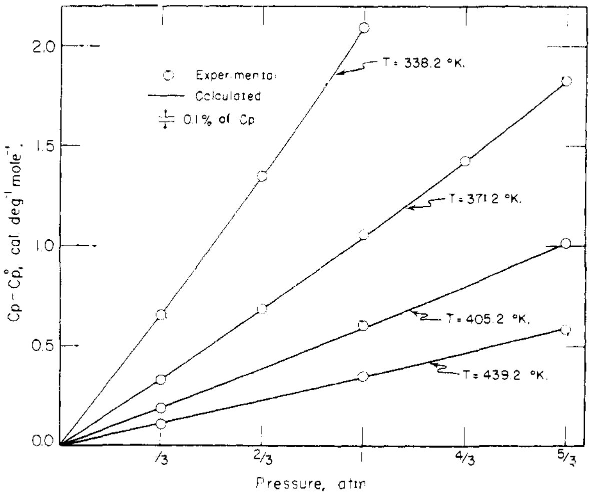

Fig. 2.—Variation with pressure of the molal heat capacity of acetone vapor.

The Second Virial Coefficient from Heats of Vaporization.—The data given above for the heat of vaporization provide, through the Clapeyron relation, a means of obtaining values of the second virial coefficient when suitable vapor pressure data are available. For this purpose the data of Zmaczynski[13] were selected as the most reliable. Zmaczynski used a twin ebulliometric system in which the boiling points of acetone and water were determined when both were boiling under a common pressure. These boiling point data were used in conjunction with the vapor pressure of water as reported by Osborne, Stimson and Ginnings[14] to obtain an Antoine equation

$$\log_{10} P = 7.12926 - 1214.516/(t + 229.745) \quad (4)$$

where P is in mm. and t is in degrees Celsius. A least-squares procedure was employed in which each point was given equal weight, but the sum of squares of the percentage deviations of calculated pressures was minimized. The maximum deviation of eq. 4 in the experimental range from 355 to 2026 mm. is 0.02% in the pressure.

Presented in Table III are values of the second virial coefficient calculated with the Clapeyron relation from heats of vaporization of eq. 1 and vapor pressure information from eq. 4. The other values of the second virial coefficient reported in Table III were obtained by Rowlinson[15] from direct pressure–volume–temperature observations.

Intermolecular Potential Energy in Acetone Vapor.—The values of $-TB''$ and B given in Tables I and II were correlated[16] to obtain the parameters

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(11) J. P. McCullough, R. E. Pennington and G. Waddington, THIS JOURNAL, **74**, 4439 (1952).

(12) (a) W. Weltner, Jr., and K. S. Pitzer, *ibid.*, **73**, 2606 (1951); (b) G. M. Barrow, *J. Chem. Phys.*, **20**, 1739 (1952).

(13) A. Zmaczynski, *J. chim. phys.*, **27**, 501 (1930).

(14) N. S. Osborne, H. F. Stimson and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 261 (1939).

(15) J. S. Rowlinson, *Trans. Faraday Soc.*, **45**, 974 (1949).

(16) The tables of functions given by J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley and Sons, New York, N. Y., 1954, p. 1147–53, and D. R. Douslin and G. Waddington, *J. Chem. Phys.*, **23**, 2453 (1955), were employed.

TABLE III

THE MOLAL SECOND VIRIAL COEFFICIENT OF ACETONE IN Cc.

T, °K.	B (obsd.)	B (calcd.)
300.4	−2030[a]	−1990
303.2	−1860[b]	−1910
317.9	−1580[a]	−1580
323.2	−1560[b]	−1480
329.3	−1370[a]	−1380
337.3	−1230[a]	−1260
343.2	−1280[b]	−1190
345.0	−1130[a]	−1160
363.2	−1040[b]	− 980
383.2	− 850[b]	− 830
403.2	− 700[b]	− 700

[a] Calculated with the Clapeyron equation. [b] Reported by Rowlinson, ref. 15.

of a Stockmayer potential function.[17] Rowlinson[15] also has given values of these parameters as determined on the basis of his data alone, but a later-reported value of the dipole moment[18] has been employed here and the parameters obtained on correlating all the data are slightly different. The present results are $t = 0.9$, $E = 850$ cal. mole^{-1}, $b_0 = 70.11$ cc. mole^{-1}. Calculated values of $-TB''$ are compared with experimental observations in Table II and comparisons of the calculated and observed results for B are given in Table III and Fig. 3. Although the deviations between calculated and observed results are in some cases on the borderline of experimental uncertainty, the representation is good considering that only two adjustable parameters are involved.

Calculation of the Thermodynamic Properties

To provide a basis for the statistical mechanical calculation of the thermodynamic functions it was necessary to: (1) compute from molecular structure data the over-all moments of inertia and the reduced moments of inertia for internal rotation; (2) obtain a vibrational assignment of the observed infrared and Raman spectral data; and (3) select a suitable barrier height to internal rotation to give agreement between calculated and experimental thermal data. The problem was complicated by the fact that one of the fundamental frequencies was not observed in the reported spectral data.

Rotational Constants.—Allen, Bowen, Sutton and Bastiansen[19] report the following values for the skeletal bond lengths and angles in acetone: 1.55 Å. for the C–C bond length, 1.22 Å. for the C═O bond length, and 120° for the C–C–C angle. These values are based on the assumptions of tetrahedral angles in the methyl groups and a C–H bond length of 1.10 Å. This set of structural parameters was employed in the formalized procedure of Kilpatrick and Pitzer[20] to obtain the values of 1.532×10^{-114} g.^{3} cm.^{6} for the product of the principal moments of inertia and 5.062×10^{-40} g.cm.^{2} for the reduced moments of inertia for internal rotation.

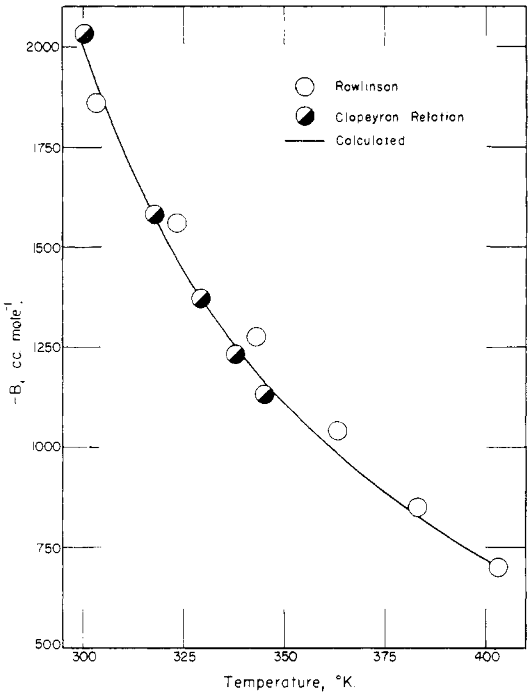

Fig. 3.—The molal second virial coefficient of acetone.

The Vibrational Assignment and Barrier to Internal Rotation.—Presented in Table IV are the selected Raman data given by Cleveland, *et al.*,[21] selected values of the reported infrared absorption frequencies,[22] and a proposed schematic assignment based on the assumption of C_{2v} symmetry for the acetone molecule. The polarization data in the Raman effect provided a useful guide for the selection of totally symmetric modes. All the observed frequencies below 1750 cm.$^{-1}$ have been assigned as fundamentals with the exception of three zero-intensity Raman lines. The two weak lines at 587 and 710 cm.$^{-1}$ have been interpreted as combinations of two of the skeletal bending frequencies with a methyl torsion level at about 200 cm.$^{-1}$. Assuming this to be the first harmonic of the torsional modes, the calculated barrier height of a simple threefold cosine potential for internal rotation is approximately 1000 cal. mole^{-1}.[23] It is shown below that the assumption of a barrier of 1000 cal. mole^{-1} for both internal rotational modes provides good agreement between the available thermal data and statistically calculated values based on this assumption. This does not preclude the possibility of a splitting of the torsional modes with a resultant average contribution to the thermodynamic functions equivalent to that calculated with a barrier of 1000 cal. mole^{-1}. However, for the present purposes of thermodynamic computations the explanation given above for the two weak Raman lines is adequate.

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(17) W. H. Stockmayer, *J. Chem. Phys.*, **9**, 398 (1941).

(18) A. D. Buckingham and R. J. W. LeFevre, *J. Chem. Soc.*, 4169 (1953), report 2.89 ± 0.02 debyes as compared with 2.74 used by Rowlinson.

(19) P. W. Allen, H. J. M. Bowen, L. E. Sutton and O. Bastiansen, *Trans. Faraday Soc.*, **48**, 991 (1952).

(20) J. E. Kilpatrick and K. S. Pitzer, *J. Chem. Phys.*, **17**, 1064 (1949).

(21) F. F. Cleveland, M. J. Murray, J. R. Coley and V. I. Komarewsky, *J. Chem. Phys.*, **10**, 18 (1942).

(22) (a) S. A. Francis, *ibid.*, **19**, 942 (1951); (b) H. W. Thompson and P. Torkington, *J. Chem. Soc.*, 640 (1945); (c) D. Price, *J. Chem. Phys.*, **9**, 725 (1914).

(23) K. S. Pitzer and W. Weltner, Jr., THIS JOURNAL, **71**, 2842 (1949), found the same barrier to internal rotation in acetaldehyde.

TABLE IV

THE VIBRATIONAL ASSIGNMENT FOR ACETONE[a]

Raman[b] ν, cm.$^{-1}$	I[c]	ρ[d]	Infrared[e] ν, cm.$^{-1}$	I[c]	Fundamental ν, cm.$^{-1}$	Designation
391	2	0.87			391	C–C–C bend, A_1
488	1	.9			488	C—C=O bend, B_1
530	3	.70	530	m	530	C—C=O bend, B_2
587	0					587 − 391 = 196
731	0					731 − 530 = 201
787	7	.20	790	w	787	C–C stretch, A_1
901	1/2		900	m	900	CH_3 rock, B_1
1066	2	.64			1066	CH_3 rock, A_1
			1095	s	1095	CH_3 rock, B_2
1221	3	.88	1218	s	1220	C–C stretch, B_1
1356	1	.6	1361	s	1360 (2)	2 sym. CH_3 def.
1423	3	.6	1415	s	1415 (2)	2 sym. CH_3 def.
1438	4		1435	s	1435 (2)	2 asym. CH_3 def.
1676	0					787 + 900 = 1688
1710	6	.38	1710	s	1710	C=O stretch, A_1
2922	10	.22	2922		2922 (2)	2 C–H stretch
2965	4	.9	2963		2965 (2)	2 C–H stretch
3005	4	.8	3008		3005 (2)	2 C–H stretch

[a] Spectra in the range from 1750 to 2900 cm.$^{-1}$ have been omitted. [b] Ref. 21. [c] Intensity; number scale 0 to 10, letter scale, weak, medium, strong. [d] Polarization ratio. [e] Ref. 22.

The assignment for the observed spectra given in Table IV leaves the A_2 methyl rocking frequency unknown. The selection rules for C_{2v} symmetry forbid the appearance of this mode in the infrared, and apparently its Raman displacement is too weak to be detected. Fortunately the heat capacity function is particularly sensitive to frequencies in this range and it was possible to determine empirically a value of 1000 cm.$^{-1}$ to provide satisfactory agreement between calculated and observed results.

The Contributions of Anharmonicity and Comparison with Experimental Data.—Simultaneously with the evaluation of the unobserved methyl rocking frequency the parameters of an empirical unharmonicity correction function were evaluated by the procedure discussed by McCullough, *et al.*[24] The parameters which provided the best fit with the experimental data are ν = 700 cm.$^{-1}$ and Z = 0.226 cal. deg.$^{-1}$ mole^{-1}. The computed anharmonicity contributions and a comparison between the calculated and calorimetric data for the heat capacity are given in Table V. Since the parameters determined for the anharmonicity function depend primarily on the variation of the heat capacity over the temperature range of experiment, it was desirable to remove the very small but unreal trend in $C_p°$ caused by the use of the International Temperature Scale. Values of the slope dT_{int}/dT[25] used to convert the experimental values of $C_p°$ to the true thermodymamic heat capacity are included in Table V.

TABLE V

CALCULATED AND OBSERVED VALUES OF THE MOLAL HEAT CAPACITY OF ACETONE IN CAL. DEG.$^{-1}$

T, °K.	dT_{int}/dT[a]	$C_p°$ (cor.)[b]	$C_p°$ (calcd.)	C_{anh}[c]
338.2	0.9999	19.48	19.48	0.05
371.2	.9997	20.83	20.83	.07
405.2	.9995	22.20	22.21	.09
439.2	.9994	23.57	23.57	.11

[a] The rate of change of International Temperature with respect to thermodynamic temperature, ref. 25. [b] Obtained from the values in Table II by multiplying by dT_{int}/dT. [c] The computed contribution of anharmonicity to the heat capacity.

Although the division of calculated contributions to the heat capacity between internal rotation, the unobserved methyl rocking frequency, and anharmonicity is somewhat arbitrary, the essentially exact agreement between calculated and observed results over a 100° temperature range indicates that no gross errors can be present. Further, the value of the entropy of liquid acetone at 298.15°K. calculated with the indicated parameters and other data given in this paper is in good accord with the experimental value of Kelley.[26] A summary of the calculations involved in this comparison is given in Table VI.

TABLE VI

THE MOLAL ENTROPY OF LIQUID ACETONE AT 298.15°K. IN CAL. DEG.$^{-1}$

$S°$	70.49[a]
Expansion to P = 0.3026 atm.[b]	2.38
Gas imperfection	− 0.22[c]
ΔS_v	−24.83[d]
S (liq.)	47.82
Third law S (liq.)	47.9 ± 0.3[e]

[a] The calculated standard entropy of gaseous acetone. [b] Calculated with eq. 4. [c] Calculated with the parameters for the second virial coefficient evaluated here and the tables of ref. 16. [d] Calculated with eq. 1. [e] Ref. 26.

The Thermodynamic Functions.—The essentially exact agreement between calculated and observed values of the vapor heat capacity and entropy indicates that the parameters employed in the statistical methanical calculations provide a sound basis for extrapolation to the other thermodynamic functions and to higher temperatures. Values of the heat capacity, entropy, enthalpy function, enthalpy and free energy function have been computed[27] at selected temperatures between 0 and 1500°K. and are presented in Table VII.

The value of the heat of combustion of acetone reported by Miles and Hunt[28] was selected as a basis for computation of the heat of formation. This value was reported in terms of a defined 15° calorie and atomic weights slightly different from those presently in use. When converted to the present thermochemical calorie (equal to 4.1840 abs. joules)

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(24) J. P. McCullough, H. L. Finke, W. N. Hubbard, W. D. Good, R. E. Pennington, J. F. Messerly and G. Waddington, THIS JOURNAL, **76**, 2661 (1954).

(25) Calculated from the equation given by J. A. Beattie, "Temperature, Its Measurement and Control in Science and Industry," Edited by H. C. Wolfe, Reinhold Publ. Corp., New York, N. Y., p. 93, 1955.

(26) K. K. Kelley, THIS JOURNAL, **51**, 1145 (1929).

(27) The vibrational contributions to the thermodynamic functions were taken from H. L. Johnston, L. Savedoff and J. Belzer, "Contributions to the Thermodynamic Functions by a Planck-Einstein Oscillator in One Degree of Freedom," NAVEXOS P-646, Office of Naval Research, Department of the Navy, Washington, D. C., 1949. Restricted internal rotation contributions were computed from the tables of K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942). The contributions of anharmonicity were calculated with the data from the tables of R. E. Pennington and K. A. Kobe, *ibid.*, **22**, 1442 (1954).

(28) C. B. Miles and H. Hunt, *J. Phys. Chem.*, **45**, 1346 (1941).

TABLE VII

THE MOLAL THERMODYNAMIC FUNCTIONS OF ACETONE IN THE IDEAL GAS STATE[a]

T, °K.	$(F° - H_0°)/T$, cal. deg.$^{-1}$	$(H° - H_0°)/T$, cal. deg.$^{-1}$	$H° - H_0°$, kcal.	$S°$, cal. deg.$^{-1}$	$Cp°$, cal. deg.$^{-1}$	$\Delta Hf°$,[b] kcal.	$\Delta Ff°$,[b] kcal.	$\log_{10} Kf$[b]
0	0	0	0	0	0	−47.74	−47.74	Infinite
273.15	−56.31	12.65	3.454	68.96	16.95	−51.40	−37.53	30.03
298.15	−57.45	13.04	3.889	70.49	17.90	−51.72	−36.30	26.61
300.00	−57.53	13.07	3.922	70.60	17.97	−51.74	−36.20	26.37
400	−61.52	14.79	5.916	76.31	22.00	−52.93	−30.84	16.84
500	−65.03	16.63	8.317	81.66	25.89	−53.94	−25.20	11.02
600	−68.22	18.47	11.084	86.69	29.34	−54.78	−19.36	7.05
700	−71.19	20.25	14.18	91.44	32.34	−55.46	−13.40	4.19
800	−74.00	21.93	17.55	95.93	34.93	−55.98	− 7.34	2.00
900	−76.67	23.51	21.16	100.18	37.19	−56.38	− 1.25	0.32
1000	−79.22	24.98	24.98	104.20	39.15	−56.61	+ 4.91	−1.08
1100	−81.68	26.34	28.98	108.02	40.85	−56.80	11.06	−2.19
1200	−84.02	27.62	33.14	111.64	42.32	−56.87	17.23	−3.14
1300	−86.28	28.80	37.45	115.08	43.61	−56.88	23.42	−3.94
1400	−88.46	29.90	41.86	118.36	44.74	−56.85	29.57	−4.62
1500	−90.54	30.92	46.38	121.46	45.72	−56.78	35.77	−5.21

[a] In order to maintain internal consistency and incremental accuracy, the values in this table are given to more significant figures than are justified by their absolute accuracy. [b] The standard heat, standard free energy, and common logarithm of the equilibrium constant for the formation of acetone by the reaction: $3C(graphite) + 3H_2(g) + {}^1/_2O_2(g) \rightarrow C_3H_6O(g)$.

and atomic weights[1] the reported value becomes 435.39 kcal. mole^{-1} for the heat of combustion of acetone in the reaction

$$C_3H_6O(g) + 4O_2(g) \longrightarrow 3CO_2(g) + 3H_2O(l)$$

taking place at 298.15°K. and a total pressure of approximately one atmosphere. Sufficient experimental details were not provided to make possible a reliable adjustment to the reaction in which all materials are in their standard states. However, the corrections involved would be small and tend to cancel one another so that for present purposes the standard heat of combustion of gaseous acetone is adopted as 435.39 kcal. mole^{-1}. This value, in conjunction with the heats of formation of water and carbon dioxide[29] yields, for the heat of formation of acetone in the reaction

$$3C(graphite) + 3H_2(g) + 1/2O_2(g) \longrightarrow C_3H_6O(g)$$

at 298.15°K. with reactants and products in their appropriate standard states, $\Delta H_f^0 = -51.72$ kcal. mole^{-1}.

The heat of formation at 298.15°K. of acetone, the thermodynamic functions in Table VII, and the thermodynamic functions of hydrogen, carbon and oxygen[29] were used to calculate values of the heat of formation, free energy of formation, and logarithm of the equilibrium constant of formation of acetone at selected temperatures from 0 to 1500°K. These data also are presented in Table VII.

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[29] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945). These data were adjusted to an atomic weight of carbon of 12.011 for use in the present calculations.

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

Concentration Dependence of the Absorption and Fluorescence Spectra of Mixed Crystals of Anthracene with Phenanthrene at 77°K.[1]

BY JEROME W. SIDMAN[2]

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The absorption and fluorescence spectra of anthracene have been studied at 77°K. in mixed crystals with phenanthrene, using concentrations of anthracene ranging from 0.6 to 100%. The origins of the absorption and fluorescence transitions vary in different ways as a function of the concentration of anthracene in the mixed crystal. The mechanism of energy transfer and fluorescence is interpreted on the basis of trapped excitons. It is postulated that the driving force for formation of the trapped exciton state in the crystal is due to the interaction of an electronically excited anthracene molecule with an unexcited anthracene molecule in an attempt to form a dimer.

Introduction

The absorption and fluorescence spectra of anthracene at low temperatures recently have been studied, both in dilute mixed crystals with naphthalene and phenanthrene[3] and in crystalline anthracene.[4] From the studies of the mixed crystal spectra,[3] it was possible to determine the symmetry properties of the lowest excited singlet state and to

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[3] J. W. Sidman, *J. Chem. Phys.*, **25**, 115 (1956).

[4] J. W. Sidman, *Phys. Rev.*, **102**, 96 (1956).