and various properties measured. A new and more convenient preparation is reported for the methyl aluminum. The others were prepared from the mercury alkyls. Considerable difficulty was experienced with the *i*-propyl compound whose preparation has not been reported previously. The melting points, densities, and other properties were measured, together with the molecular weight in benzene solution (from freezing point measurements).

Aluminum trimethyl was found to be completely dimeric in the range studied while the ethyl and *n*-propyl compounds show measurable dissociation of the dimer. On the other hand, aluminum *i*-propyl is completely monomeric. Also, a mixed methyl-*i*-propyl compound was found to be more highly dimerized than the ethyl.

After making corrections for deviations from Raoult's law, association constants were calculated for the ethyl and *n*-propyl aluminum.

Consideration of these data together with the Raman spectrum and other published information leads to the conclusion that the binding is primarily a polar attraction of the positive aluminum atoms for the negative α carbon atoms This agrees with the fact that the alkyls of metals more electropositive than aluminum are all polymerized, usually into solids, while the alkyls of more electronegative metals are monomeric.

BERKELEY, CALIF. RECEIVED JUNE 12, 1946

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF CALIFORNIA]

The Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressure, Entropy, Vibration Frequencies and Barrier to Internal Rotation of Styrene

BY KENNETH S. PITZER, LESTER GUTTMAN[*] AND EDGAR F. WESTRUM, JR.

Styrene is one of the most important polymerizing monomers and its fundamental thermodynamic properties are, therefore, of considerable interest. A preliminary summary of these values has been published.[1] The directly measured data are presented in detail in this paper. The accompanying paper presents calculated values for the thermodynamic properties of the ideal gas at higher temperatures for styrene and for its methyl derivatives.

The potential barrier to the rotation of vinyl (*vs.* the phenyl) group is also of interest because of its relation to the energy associated with the conjugation of the vinyl and phenyl groups.

Apparatus.—The calorimeter and vapor pressure apparatus have been described previously.[2] The equipment used for *m*- and *p*-xylene was employed here without change.

Material.—An Eastman Kodak Company product was distilled through a 25-plate column, under reduced pressure, directly into the calorimeter. The boiling range was less than 0.1°. A few mg. of hydroquinone was added to prevent polymerization. Two samples were used in the measurements, the first of 76.099 g., or 0.7307 mole, the second of 78.189 g., or 0.7508 mole (based on vacuum weights, and a molecular weight of 104.144). From premelting measurements, the liquid-soluble, solid-insoluble impurity was estimated to be about 0.2 mole per cent.

Melting Point.—The equilibrium temperature at various fractions melted was observed, and plotted against the reciprocal of the fraction melted (Fig. 1). Extrapolation to infinite dilution gave the true melting point as 242.47 ± 0.05°K. Wood and Higgins[3] give the value $-30.60°$ (242.56°K.).

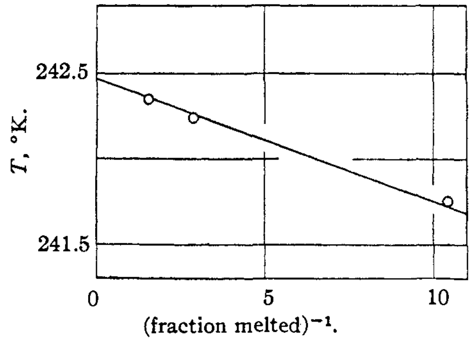


Fig. 1.—The melting point of styrene.

Heat Capacity.—The heat capacity of styrene was measured from 15° K. to room temperature, and the results, plotted in Fig. 2, are given in Table I. Values at rounded temperatures are given in Table II. The unit of energy is a defined calorie equal to 4.1833 Int. joules.

The heat capacity curve is unusual in that the solid has a larger heat capacity than the liquid at the melting point. The anomalous rise in the solid curve starts at about 140°K. which is 100° below the melting point. Presumably, it represents the beginning of a gradual or second order transition which is interrupted by the melting point. Similar behavior was observed in ethylene.[4] However, it is not obvious what the structural character of this transition might be

---

[*] Allied Chemical and Dye Corp. Fellow, 1942–43.

[1] L. Guttman, E. F. Westrum, Jr., and K. S. Pitzer, THIS JOURNAL, 65, 1246 (1943).

[2] K. S. Pitzer and D. W. Scott, *ibid.*, 65, 803 (1943).

[3] L. A. Wood and C. F. Higgins, *India Rubber World*, 107, 475 (1943).

[4] C. J. Egan and J. D. Kemp, THIS JOURNAL, 59, 1264 (1937).

since these molecules could hardly be starting to rotate in the crystal.

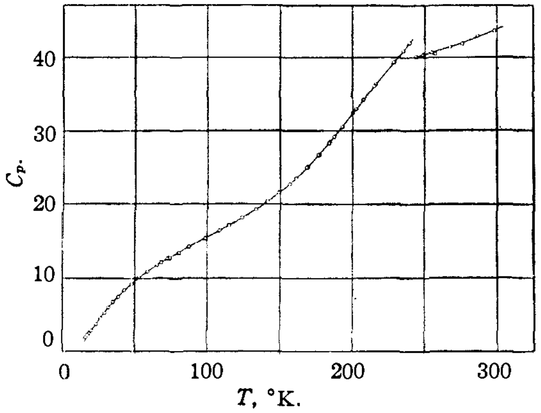


Fig. 2.—The heat capacity of styrene in cal. per degree mole.

The amount of premelting appeared to depend on the temperature to which the sample had been previously cooled, and Raoult's law was not well obeyed, as was to be expected, if the impurity were a high polymer. The points marked [a] were obtained by a reasonable extrapolation of the heat capacity, attributing extra heat to premelting. Fitting a quadratic equation to the observed liquid heat capacity gave the result

$$C_p = 41.85 + 0.06640t + 0.00030692t^2$$

with t in degrees Centigrade.

Heat of Fusion.—Four determinations of the heat of fusion were made in the usual manner, and the results are given in Table III. The correction for heat interchange by radiation during the heating period is considerable at this comparatively high temperature, but we were unable to make it as accurately as in certain other cases because this calorimeter had no outside thermometer. The large fluctuations are due mainly to this cause. Our value of 2617 cal./mole may be compared to 2645 cal./mole given by Wood and Higgins.[3]

Vapor Pressure.—These measurements were complicated by some polymerization at the higher temperatures. The values least affected by polymerization are given in Table IV. The order of measurement was 12.5, 25, 50, 60, 37.5°. The temperature was then brought back to 25° and values 0.1 mm. lower were obtained.

In fitting an equation to these values, the difference in heat capacity between the vapor and liquid, −14 cal./degree mole, given from other measurements was assumed. Then equation (1) was obtained

$$\log p_{\text{mm.}} = 28.8631 - 3203/T - 7 \log T \quad (1)$$

on the basis that the measured pressures at the higher temperatures are slightly too low because of polymerization. Patnode and Schreiber[5] considered a wide range of vapor pressure data and derived the following equation

$$\log p = 7.2788 - 1649.6/(t + 230) \quad (2)$$

TABLE I

HEAT CAPACITY OF STYRENE

All runs below 150°K. are series I; all above 200°K. are series II, unless otherwise indicated, between 150 and 200°K., series is indicated by Roman numeral.

T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.
15.28	1.635	80.47	13.46	II 193.19	30.56[a]
16.42	1.905	87.52	14.23	II 200.38	32.47[a]
17.68	2.235	98.77	15.38	II 202.56	32.97[a]
19.02	2.558	108.46	16.40	207.77	34.28[a]
20.40	2.894	115.12	17.12	215.39	36.12[a]
23.42	3.732	124.08	18.15	216.50	36.36[a]
26.59	4.560	133.15	19.25	228.86	39.38[a]
29.17	5.240	141.08	20.34	235.64	41.01[a]
31.98	5.989	I 149.12	21.54	240.03	42.06[a]
35.08	6.666	I 156.72	22.76	Melting point	
38.67	7.431	I 161.16	23.52	246.73	40.18
42.89	8.318	II 168.49	25.00	248.98	40.41
47.77	9.119	I 169.39	25.06	249.91	40.44
52.91	10.02	II 176.70	26.72	I 255.15	40.72
58.95	10.84	I 177.08	26.71	257.54	40.57
65.58	11.75	I 183.95	28.30	267.72	41.48
68.34	12.13	II 184.52	28.52	276.24	41.97
72.65	12.65	II 187.51	29.20	286.71	42.91
74.20	12.75	I 193.09	30.58	298.54	43.64

TABLE II

HEAT CAPACITY OF STYRENE AT ROUNDED TEMPERATURES

T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.
15	1.565	150	21.69
20	2.798	160	23.32
25	4.134	170	25.25
30	5.516	180	27.44
35	6.649	190	29.80
40	7.715	200	32.36
45	8.726	210	34.81
50	9.574	220	37.22
60	11.02	230	39.66
70	12.30	240	42.06
80	13.43	Melting point	
90	14.49	250	40.48
100	15.50	260	41.03
110	16.56	270	41.65
120	17.67	280	42.32
130	18.85	290	43.06
140	20.19	300	43.86

TABLE III

HEAT OF FUSION OF STYRENE

Units are cal./mole throughout

Time, min.	Cor. heat input	$\int C_p\,dT$	Pre-melting	ΔH
29	3149.4	544.1	23.1	2628.4
41	3580.3	958.5	2.8	2624.6
31	2986.2	382.1	4.7	2608.8
34	3152.4	546.3	10.2	2616.3

Weighted mean 2617 ± 15 cal./mole

[5] Patnode and Schreiber, THIS JOURNAL, 61, 3449 (1939).

Values calculated from equation (2) are also shown in Table IV and are seen to be higher by one or two tenths mm. than our observations. While it is believed that our values are more accurate at the lower temperatures, at 60° we favored the higher value and fitted equation (1) to it.

TABLE IV

VAPOR PRESSURE OF STYRENE

t, °C.	P, mm. of Hg Exp.	Eq. (1)	Eq. (2)
12.5	2.88	2.88	2.99
25.0	6.31	6.30	6.45
37.5	12.71	12.79	12.94
50.0	24.23	24.30	24.40
60.0	38.83	38.95	38.95

For the heat of vaporization at 298.16°K., equation (1) yields 10,500 ± 100 cal./mole if (PV/RT) is assumed to be 0.999. This heat of vaporization is 110 cal. higher than the value given previously.[1]

The Entropy from Calorimetric Data.—The heat capacity from 15 to 27°K. was fitted by a Debye function for six degrees of freedom, and this was used for the small extrapolation below the lowest temperature of measurement. The calculation of the entropy of styrene is summarized in Table V.

TABLE V

ENTROPY OF STYRENE FROM CALORIMETRIC DATA

0–15°K., 2 × $D(123/T)$	0.56 cal./deg. mole
15–242.47°K., graphical	36.82
Fusion, 2617/242.47	10.79
242.47–298.16°K., graphical	8.61
Liquid at 298.16°K.	56.78 ± 0.3
Vaporization, 10500/298.16	35.22
Compression, R ln (6.30/760)	−9.52
Ideal gas at 298.16°K. and 1 atm.	82.48 ± 0.5

Molecular Vibration Frequencies.—In order to make statistical mechanical calculations for styrene an assignment of vibration frequencies was attempted. It is based on the Raman[6] and the infra-red[7] spectra of styrene with guidance from the assignments for toluene[2] and propylene.[8] The correlation with the assignments of the related molecules is surprisingly good, which gives us considerable confidence in the results as given in Table VI. However, certain particular frequencies are subject to considerable doubt; indeed, the toluene assignment itself is far from certain in each detail. Nevertheless, the results of statistical calculations based on these frequencies should be reasonably reliable.

TABLE VI

VIBRATION FREQUENCIES OF STYRENE

Symmetry class[b]	No.	Toluene / Propylene	Styrene[a]		
A′	1	1002	999	R	
	2	(3062)	(3062)		
	3	1282	1280		IR
	6a	521	510	R	
	6b	622	622	R	
	7a	1210	1204	R	IR
	7b	(3047)	(3047)		
	8a	1603	1601	R	IR
	8b	1586	1581	R	IR
	9a	1175	1181	R	...
	9b	1155	1155	R	IR
	12	785	777	R	IR
	13	(3046)	(3046)		
	14	1630	(1640)		
	15	1070	1070	..	IR
	18a	1030	1030	R	IR
	18b	340	240	R	
	19a	1483	1495	R	IR
	19b	1310	1320	R	...
	20a	(3080)	(3080)		
	20b	(3080)	(3080)		
	νC=C	1647	1636	R	IR
	δCH	1297	1301	R	...
	δCH_2(s)	1416	1415	R	IR
	δCH_2(a)	1172	(1172)		
	νCH	(3050)	(3050)		
	νCH_2(s)	(3050)	(3050)		
	νCH_2(a)	(3050)	(3050)		
	δC—C=C	417	442	R	
A″	4	695	(690)	..	IR
	5	943	(940)	..	...
	10a	842	835	R	IR
	10b	730	730	..	IR
	11	216	212	R	
	16a	405	416	R	
	16b	467	442	R	
	17a	(985)	988	R	
	17b	890	(900)		
	δCH	990	990		IR
	δCH_2	911	908	R	IR
	torsC=C	578	560	R	

[a] R indicates observed in the Raman spectrum; IR indicates observed in the infra-red spectrum. [b] A′ comprises motions in the plane of the molecule. A″ comprises motions perpendicular to the plane of the molecule. (s) and (a) refer to symmetric and antisymmetric, respectively.

Statistical Calculations.—The moments of inertia were calculated from the following distances and angles: C–C aromatic 1.39 Å., C–H ar. 1.08, C aromatic–C olefin 1.455, C–H olefin 1.071, all angles 120°. It is presumed that the conjugation of the double bonds tends to keep all carbon atoms co-planar. The moments of

---

(6) Bourguel, *Compt. rend.*, **194**, 1736 (1932); **195**, 311 (1932); Lespieau and Bourguel, *Bull. soc. chim.*, **47**, 1365 (1930); Lespieau and Bourguel, *Compt. rend.*, **190**, 1504 (1930); Mizushima, Morino and Inoue, *Bull. Chem. Soc. Japan*, **12**, 136 (1937).

(7) D. Williams, *Physics*, **7**, 399 (1936); R. Stair and W. W. Coblentz, *J. Research, Natl. Bur. Standards*, **15**, 295 (1935); Spectrograms from the Mellon Institute and Dow Chemical Co. distributed by American Petroleum Institute Project 44 at the Natl. Bur. of Standards.

(8) E. B. Wilson, Jr., and A. J. Wells, *J. Chem. Phys.*, **9**, 319 (1941); J. E. Kilpatrick and K. S. Pitzer, to be published.

inertia for that configuration are 16.39, 51.53, 67.92, each × 10^{-39} g. sq. cm., for over-all rotation and the reduced moment of inertia for internal rotation is 19.97 × 10^{-40} g. sq. cm. The axis of smallest inertia makes an angle of 12.5° with the axis of internal rotation. Since this molecule can be described as a balanced top (the phenyl group) attached to a rigid frame, the tables of Pitzer and Gwinn[9] are applicable for internal rotation if the potential energy has the simple cosine form. On this basis, one finds that a potential barrier of 2200 cal. per mole restricts the internal rotation in styrene. Table VII gives the details of this calculation. Some further thermodynamic quantities are given in an accompanying paper.

TABLE VII

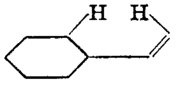
CALCULATION OF THE POTENTIAL BARRIER FROM THE ENTROPY OF STYRENE GAS

(T = 298.16°K., hypothetical perfect gas at 1 atm.)

	S
Translation and over-all rotation	67.68
Vibration	10.11
Free internal rotation	5.72
	83.51
Experimental	82.48
$(S_f - S)$	1.03
$1/Q =$	0.0928
$V/RT =$	3.71
$V =$	2.2 kcal./mole

Discussion

The conjugation of the vinyl and phenyl groups in styrene requires coplanarity of these groups; consequently, the potential barrier of 2.2 kcal. per mole to the rotation of one group with respect to the other is a measure of the energy of this conjugation. However, there are several complications in this interpretation. There is undoubtedly some interference between the hydrogen atoms in the ortho position and the *cis*-beta position as indicated in the diagram.



In this connection we may remark that Aston, Szasz, Woolley and Brickwedde[10] calculate that the *cis* orientation in butadiene is 2.3 kcal. per mole higher in energy than the *trans* configuration. The *cis* configuration involves an interference similar to that in styrene. However, the butadiene data are subject to interpretation in other ways so that this value cannot be given very great weight.

Another complication is the hyperconjugation or second order conjugation[11] still present when the vinyl group is perpendicular to the phenyl group. This might be of a magnitude similar to that in propylene or around 2 kcal. per mole (Mulliken gives 1.3 kcal. but the heat of hydrogenation of propylene[12] is about 2.5 kcal. less than that of ethylene).

The heat of hydrogenation of styrene[13] is 4.9 kcal. per mole less than the sum for benzene and ethylene. Thus, if one assumes that any steric interferences in styrene are offset by similar strains in ethylcyclohexane and ignores energy irregularities in the saturated molecules, one would obtain 4.9–2.2 or 2.7 kcal. of second order conjugation energy in styrene when the vinyl is perpendicular to the phenyl group. From the discussion above this result is reasonable but the numerous assumptions in the calculation leave some doubt as to its meaning. However, it seems safe to conclude that the first order conjugation energy of styrene is approximately 5 kcal. plus the energy of the hydrogen interference. The latter term might be as large as two or three kcal. giving a total range from 5 to 8 kcal. per mole for the conjugation energy.

Acknowledgment.—We wish to thank Dr. Charles Beckett for revising our older statistical calculation to include certain recent data.

Summary

The heat capacity of solid and liquid styrene was measured from 14 to 300°K. and the heat of fusion found to be 2617 cal./mole at 242.47°K. (the melting point). The vapor pressure was measured from 0 to 60° and from it the heat of vaporization calculated to be 10,500 cal./mole at 25°. The entropy at 298.16°K. calculated to be 56.78 cal./deg. mole for the liquid and 82.48 cal./deg. mole for the hypothetical ideal gas at 1 atm.

An assignment of the vibration frequencies was made and the entropy calculated from statistical mechanics. It was necessary to assume a 2200 cal./mole potential barrier to obtain agreement with the experimental value. The meaning of this barrier in terms of conjugation or resonance energy is discussed.

BERKELEY, CALIFORNIA RECEIVED JUNE 24, 1946

---

[9] K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942); K. S. Pitzer, *ibid.*, **14**, 139 (1946).

[10] J. G. Aston, G. Szasz, H. W. Woolley and F. G. Brickwedde, *J. Chem. Phys.*, **14**, 67 (1946).

[11] R. S. Mulliken, C. A. Rieke and W. G. Brown, THIS JOURNAL, **63**, 41 (1941).

[12] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *ibid.*, **57**, 65, 876 (1935); **58**, 137 (1936).

[13] M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky and W. E. Vaughan, *ibid.*, **59**, 831 (1937).