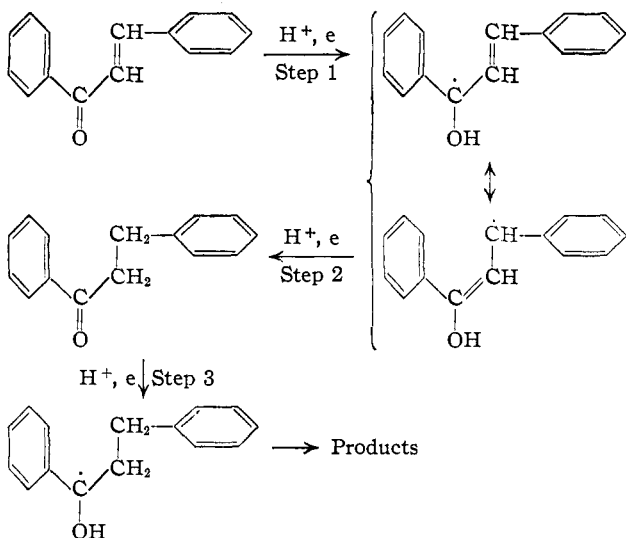


that the third wave represents the reduction of a substance which no longer possesses an  $\alpha,\beta$ -unsaturated carbonyl system, but which contains a structural element such as a carbonyl group attached to an aromatic ring. This supposition is supported by the observation that the third wave occurs at  $E_{1/2}$  values in the range of those reported by Scaramelli<sup>12</sup> for hydroxylated acetophenone derivatives. The values in Table V show this correspondence.

From the considerations of the foregoing discussion, the following sequence of steps at the electrode can be suggested (using chalcone as a typical example).



This sequence of electrode reactions makes it possible to account for the occurrence of three

waves, and also for the considerably greater ease of reduction of chalcones than of similarly substituted flavones and flavanones. If one compares the considerably greater possibility for resonance stabilization of the initial free radical, as compared with the original chalcone, with the corresponding differences between the unreduced and free-radical forms of flavones and flavanones, it is seen that the chalcone free radical is *preferentially* stabilized to the greatest degree, that of a flavone next, and that of a flavanone least. This is completely in accord with the relative ease of reduction at the electrode of chalcone > flavone > flavanone.

### Summary

A study has been made of the effect of substitution of hydroxyl, alkoxy and acetoxy groups upon the ease of reduction of a group of flavones, flavanones and chalcones at the dropping-mercury electrode. When these groups are present in positions conjugated with the carbonyl groups in these compounds, hydroxyl and methoxy groups decrease, and acetoxy groups increase, the ease of reduction.

The results have been interpreted in terms of one-electron electrode reactions and the relative stabilities of the unreduced compounds and the initial free radicals produced in the first stage of the electrode process.

Flavanones give single-wave, flavones double-wave and chalcones triple-wave polarograms. It is suggested that these behaviors are due to the successive reduction at the electrode of the unreduced compound and one-electron-reduced intermediates.

LOS ANGELES, CALIFORNIA

RECEIVED JULY 5, 1949

[CONTRIBUTION No. 17 FROM THE THERMODYNAMICS LABORATORY OF THE PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

## Experimental Vapor Heat Capacities and Heats of Vaporization of 2-Methylpentane, 3-Methylpentane and 2,3-Dimethylbutane<sup>1</sup>

BY GUY WADDINGTON, J. C. SMITH,<sup>2</sup> D. W. SCOTT AND H. M. HUFFMAN

This paper is a further contribution from the thermodynamic research program of the Petroleum and Natural-Gas Branch of the Bureau of Mines. The vapor heat capacities and heats of vaporization of 2,2-dimethylbutane and *n*-hexane have already been measured in this Laboratory.<sup>3</sup> Similar data for the three remaining hexanes are presented here. In the case of the heat-capacity measurements, the temperature range was from approximately the normal boiling point of the compound to 200°. Heats of vaporization were

determined at temperatures corresponding to saturated pressures of about one-quarter, one-half and one atmosphere.

### Experimental

**Apparatus and Method.**—Since the apparatus and experimental procedures used were essentially as described in detail in an earlier paper,<sup>4</sup> only a brief account of them will be given here.

A measured, constant flow of hydrocarbon vapor was produced by electrical heating in a cycling vaporizer. This was passed through a flow calorim-

(1) Not subject to copyright.

(2) Present address: Army Chemical Center, Edgewood, Maryland.

(3) Waddington and Douslin, *THIS JOURNAL*, **69**, 2275 (1947).

(4) Waddington, Todd and Huffman, *ibid.*, **69**, 22 (1947).

eter in which the temperature rise, produced in the vapor by a measured power input, was measured by means of platinum resistance thermometers. The apparent heat capacity of the vapor,  $C_{p(\text{app.})}$  is given by  $W/F\Delta T$  where  $W$  is the power supplied to the calorimeter,  $F$  is the flow per unit of time and  $\Delta T$  is the observed temperature rise. Heat losses from the calorimeter are such that  $C_{p(\text{app.})} = C_p + k/F$  where  $C_p$  is the true heat capacity. Hence, by measuring apparent heat capacities at several flow rates, then plotting  $C_{p(\text{app.})}$  vs.  $1/F$  and extrapolating to zero value of  $1/F$ , corrected values of  $C_p$  are obtained. The heat-capacity data are believed accurate to  $\pm 0.2\%$ . By measuring heat capacities at two or more pressures and extrapolating linearly to zero pressure the heat capacity of the ideal gas is obtained.

The proportionality between flow of vapor and electrical energy supplied to the vaporizer was determined by condensing and weighing the vapor produced, by a measured power input, during a measured time interval. This measurement, when properly corrected,<sup>4</sup> yields heats of vaporization believed to be accurate to about  $\pm 0.1\%$ .

The apparatus, as originally described,<sup>4</sup> has been modified slightly. The *aneroid* manostat<sup>5</sup> now used gives good control, and with it small or large changes of the pressure setting can be made very conveniently. The measurement of time has been made more accurate by use of fifty cycle alternating current obtained from a General Radio 816A Precision Tuning Fork Unit and a special power amplifier.

**Materials.**—The 2-methylpentane was Phillips Technical Grade, which, by a preliminary distillation for other purposes, had been brought to a purity of approximately 98 mole per cent. Further distillation in a 100-plate column, at an initial reflux ratio of 140:1 and a final reflux ratio of 90:1, resulted in a material having the following properties:  $d^{20}_4$  0.6531,  $n^{20}_D$  1.37145. The purity, determined from a melting curve, assuming liquid-soluble, solid-insoluble impurities, was 99.88 mole per cent.

The 3-methylpentane was also Phillips Technical Grade, which was purified by distillation at the Laramie Station of the Petroleum and Natural-Gas Branch of the Bureau of Mines. Since attempts to crystallize 3-methylpentane have not been successful, an analysis by means of the freezing behavior was impossible. By analogy with a sample of 2-methylpentane having a similar history, it is believed that the material used had a purity greater than 98 mole per cent. It had the following properties:  $d^{20}_4$  0.6644,  $n^{20}_D$  1.37647.

The 2,3-dimethylbutane was Phillips Pure Grade. It was purified further by distillation in a 100-plate column at a reflux ratio of 100:1. The purity estimated from a freezing curve was 99.87

mole %. It had the constants  $d^{20}_4$  0.6616,  $n^{20}_D$  1.37501. Whenever air had access to this compound, it was protected from peroxide formation by the addition of about 0.02 per cent. of a commercial anti-oxidant known as "tri-alkyl phenol."

**Heats of Vaporization.**—Table I gives a summary of the heats of vaporization of the three compounds investigated. For each compound, there is available for comparison an accurate value at 25° from the work of Osborne and Ginnings.<sup>6</sup> The largest difference observed, six calories at 25° for 2-methylpentane, is within the estimated  $\pm 0.1\%$  uncertainty of the present work. The values reported by Lemons with Felsing<sup>7</sup> tend, as in the case of *n*-hexane, to be approximately 1% lower than the values here reported.

TABLE I  
HEATS OF VAPORIZATION OF 2-METHYLPENTANE, 3-METHYLPENTANE AND 2,3-DIMETHYLBUTANE

$t$ , °C.	Number of expts.	$\Delta H_{\text{vapn.}}$ cal./mole <sup>a</sup>	$\Delta H_{\text{vapn.}}$ equation
2-Methylpentane			
25.0 <sup>b</sup>	..	7138	7141
25.0	3	7144 $\pm$ 2 <sup>b</sup>	7141
45.0	2	6865 $\pm$ 1	6856
60.3	3	6642 $\pm$ 2	6643
3-Methylpentane			
25.0 <sup>b</sup>	..	7235	7236
30.1	3	7170 $\pm$ 2	7169
50.6	3	6890 $\pm$ 3	6890
63.3	3	6711 $\pm$ 4	6707
2,3-Dimethylbutane			
22.80	3	6988 $\pm$ 3	6987
25.00 <sup>b</sup>	..	6960	6960
29.87	2	6900 $\pm$ 2	6899
39.97	3	6769 $\pm$ 5	6770
57.99	3	6519 $\pm$ 6	6521

<sup>a</sup> 1 cal. = 4.1833 int. joules; at. wt. carbon = 12.01; at. wt. hydrogen = 1.008. <sup>b</sup> Maximum deviations from the mean.

For interpolation to intermediate temperatures, the following equations may be used without significant loss of accuracy:

$$2\text{-methylpentane: } \Delta H_{\text{vap.}} = 9173 - 0.2673T - 0.02196T^2$$

$$3\text{-methylpentane: } \Delta H_{\text{vap.}} = 9688 - 3.366T - 0.01629T^2$$

$$2,3\text{-dimethylbutane:}$$

$$\Delta H_{\text{vap.}} = 8461 + 2.233T - 0.02438T^2$$

The last column of Table I lists values calculated with these equations.

**Vapor Heat Capacities.**—The molal vapor heat capacity of each compound was measured at five temperatures ranging from slightly below the normal boiling point to approximately 200°. At each temperature, measurements were made at two and, in some cases, three pressures. Table II summarizes the experimental values.

(6) Osborne and Ginnings, *J. Research Natl. Bur. Standards*, **39**, 453 (1947).

(7) J. F. Lemons with W. A. Felsing, *THIS JOURNAL*, **65**, 46 (1943).

(5) Manufactured by Wallace and Tiernan Products, Inc., Belleville, N. J.

TABLE II  
EXPERIMENTAL VAPOR HEAT CAPACITIES, CAL./DEG./MOLE

$T, ^\circ\text{K.} \rightarrow$ $P., \text{mm.}$	325.10	362.15	402.25	436.20	471.15
		2-Methylpentane			
760.5		41.02	44.48	47.43	50.35
455.4	37.45	40.72			
211.9	37.10	40.51	44.21	47.24	50.23
		3-Methylpentane			
$T, ^\circ\text{K.} \rightarrow$ $P., \text{mm.}$	332.10	367.55	402.35	436.20	471.15
760.3		40.80	43.82	46.77	49.74
499.5	37.49	40.62			
235.8	37.16	40.42	43.55	46.60	49.61
		2,3-Dimethylbutane			
$T, ^\circ\text{K.} \rightarrow$ $P., \text{mm.}$	341.60	371.20	402.30	436.00	471.15
760.0	38.62	41.19	43.98	46.94	49.90
284.4	38.10	40.88	43.77	46.81	49.82

**Heat Capacity in the Ideal Gas State.**—From the data given in Table II, values of the heat capacity of the ideal gas were obtained at each temperature by plotting  $C_p$  vs.  $P$  and extrapolating to zero pressure. The validity of the linear extrapolation over the pressure range studied has been verified by determining heat capacities at three different pressures for *n*-hexane,<sup>8</sup> *n*-heptane<sup>4</sup> and benzene<sup>8</sup> in addition to two of the three compounds reported here. Wacker, Cheney and Scott<sup>9</sup> have also demonstrated this point in the case of isobutane at  $-30.0^\circ$ .

TABLE III  
HEAT CAPACITIES IN THE IDEAL GAS STATE, CAL./DEG./MOLE

$T, ^\circ\text{K.}$	$C_p^1$	$C_p^0$	$C_p^1 - C_p^0$ , cal./deg./mole		
			Expt.	2nd Virial	Berthelot
		2-Methylpentane			
325.10	37.91	36.77	1.14	1.28	0.68
362.15	41.01	40.30	0.71	0.69	.49
402.25	44.48	44.08	.40	.40	.36
436.20	47.42	47.14	.28	.27	.28
471.15	50.34	50.16	.18	.18	.22
		3-Methylpentane			
332.10	(37.80)	36.88	0.92	0.94	0.57
367.55	40.80	40.25	.55	.56	.42
402.35	43.81	43.43	.38	.37	.32
436.20	46.77	46.52	.25	.26	.25
471.15	49.74	49.55	.19	.19	.20
		2,3-Dimethylbutane			
341.60	38.62	37.78	0.84	0.81	0.51
371.20	41.19	40.69	.50	.50	.40
402.30	43.98	43.63	.35	.32	.31
436.00	46.93	46.73	.20	.21	.25
471.15	49.90	49.77	.13	.14	.19

(8) Scott, Waddington, Smith and Huffman, *J. Chem. Phys.*, **15**, 565 (1947).

(9) Paul F. Wacker, Ruth K. Cheney and Russell B. Scott, *J. Research Natl. Bureau of Standards*, **38**, 651 (1947).

Values of  $C_p^0$ , the heat capacity of the ideal gas, are summarized for the three compounds in Table III. Over the temperature range of the experiments, the following empirical equations represent the experimental results without significant loss of accuracy. The maximum deviations of the experimental points from the empirical equations are given in parentheses.

2-methylpentane: ( $\pm 0.06\%$  341 – 471°K.)

$$C_p^0 = 1.55 + 0.11963 T - 3.478 \times 10^{-6} T^2$$

3-methylpentane: ( $\pm 0.04\%$  332 – 471°K.)

$$C_p^0 = 1.40 + 0.11776 T - 3.291 \times 10^{-6} T^2$$

2,3-dimethylbutane: ( $\pm 0.02\%$  325 – 471°K.)

$$C_p^0 = -2.65 + 0.13692 T - 5.433 \times 10^{-6} T^2$$

Figure 1 shows differences between the ideal gas heat capacities of the isomeric hexanes. Data used in this plot are from the present work and from earlier published work<sup>8</sup> from this Laboratory. Over the temperature range studied, differences between the heat capacities of the isomers do not exceed 2%.

Pitzer and Kilpatrick<sup>10</sup> have calculated heat capacities of the ideal gas for the isomeric hexanes by approximate statistical methods. The results so obtained have received wide distribution in the tables published under the auspices of API Project 44<sup>11</sup>; hence it is of interest to compare the calculated values with those obtained experimentally. Table IV makes this comparison at two temperatures. In most cases the calculated results are higher than the experimental values by amounts larger than the estimated accuracy uncertainty of the latter. However, the absence of any gross discrepancies will increase confidence in the extensive compilations of statistically calculated vapor heat capacities<sup>11</sup> where no experimental checks exist.

TABLE IV  
CALCULATED AND OBSERVED IDEAL-GAS HEAT CAPACITIES OF THE HEXANES, CAL./MOLE/DEG.

	373.16°K.			473.16°K.		
	Calcd.	Obsd.	$\Delta$	Calcd.	Obsd.	$\Delta$
<i>n</i> -Hexane	41.70	40.96	0.74	50.24	49.84	0.40
2-Methylpentane	41.53	41.35	.18	50.32	50.37	-.05
3-Methylpentane	42.22	40.76	1.46	50.84	49.75	1.09
2,2-Dimethylbutane	41.71	41.22	0.49	50.84	50.43	0.41
2,3-Dimethylbutane	41.80	40.88	.92	50.58	49.97	.61

#### Second Virial Coefficients from Thermal Data.

—From the heats of vaporization and from published vapor-pressure data<sup>12</sup> molal volumes of the vapor were calculated at several temperatures for each compound by use of the exact Clapeyron equation  $\Delta H_{\text{vap.}} = T(V_g - V_l) dP/dT$ , in which  $V_g$  and  $V_l$  indicate molal volumes of vapor and liquid, respectively. Further information concerning vapor volumes as a function of tempera-

(10) Pitzer and Kilpatrick, *Chem. Revs.*, **39**, 435 (1946).

(11) American Petroleum Institute Research Project 44 at the National Bureau of Standards, Selected Values of Properties of Hydrocarbons, Table 2v (Part I) September 30, 1944; November 30, 1946.

(12) C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 219 (1945).

TABLE V  
 CALCULATED AND OBSERVED VIRIAL COEFFICIENTS

2-Methylpentane			3-Methylpentane			2,3-Dimethylbutane		
$T, ^\circ\text{K.}$	$B, \text{cc. Obsd.}$	$B, \text{cc. Calcd.}$	$T, ^\circ\text{K.}$	$B, \text{cc. Obsd.}$	$B, \text{cc. Calcd.}$	$T, ^\circ\text{K.}$	$B, \text{cc. Obsd.}$	$B, \text{cc. Calcd.}$
298.16	-1712	-1753	298.16 <sup>a</sup>	-1718	-1662	295.96	-1554	-1592
298.16 <sup>a</sup>	-1792	-1753	303.26	-1592	-1600	298.16 <sup>a</sup>	-1569	-1557
318.16	-1487	-1485	323.71	-1418	-1408	303.03	-1496	-1500
333.43	-1332	-1330	336.45	-1285	-1308	313.13	-1400	-1388
						331.15	-1256	-1233

<sup>a</sup> Heat of vaporization from ref. 6.

ture was supplied by the fact that the experimentally determined values of  $(\partial C_p/\partial P)_T$  are equal to  $-T(\partial^2 V/\partial T^2)_P$ . The two types of thermal data were correlated by means of the following empirical relations for the second virial coefficient  $B$  (defined by  $PV = RT + BP$ ).

2-Methylpentane;  $B = -390 - 40.26e^{1050/T}$  cc.

3-Methylpentane;  $B = -318 - 91.9e^{800/T}$  cc.

2,3-Dimethylbutane;  $B = -526 - 21.9e^{1160/T}$  cc.

The parameters were evaluated by previously reported methods.<sup>8</sup>

Table V gives data for 2-methylpentane, 3-methylpentane and 2,3-dimethylbutane which illustrate the correlations obtainable by use of these expressions for the second virial coefficients. In all cases differences between the observed and calculated values of  $B$  correspond to combined errors in the experimental values of  $\Delta H_{\text{vap}}$ , and  $dP/dT$  of less than 0.1%. Reference to the last three columns of Table III further illustrates the correlations obtainable with the expressions for the second virial coefficients and also calls attention to the errors to which the Berthelot equation of state leads in calculating  $C'_p - C''_p$  in the region of the normal boiling point.

Kay<sup>18</sup> has made direct determinations of the densities of the isomeric hexanes from the normal boiling points to the critical temperatures. Table VI makes a comparison, at two temperatures, of Kay's data and vapor densities calculated from second virial coefficients. At the lower temperature, which is slightly above the normal boiling point, the agreement is within the  $\approx 0.0002$  g./cc. which Kay<sup>14</sup> assigns to his work. In this region the use of the second virial coefficient might be expected to give more accurate results. The results at the higher temperature involve a considerable extrapolation of both temperature and pressure in the use of the second virial coefficients and yet the agreement is fair. The available evidence (see also ref. 8) suggests that second virial coefficients

 TABLE VI  
 SATURATED VAPOR DENSITIES, G./CC.

	70°C.		150°C.	
	Kay	Virial	Kay	Virial
2-Methylpentane	0.0042	0.00430	0.0283	0.0283
2-Methylpentane	.0040	.00408	.0254	.0261
2,3-Dimethylbutane	.0048	.00468	.0290	.0287

(13) Kay, THIS JOURNAL, **68**, 1336 (1946).

(14) Kay, *ibid.*, **69**, 1273 (1947).

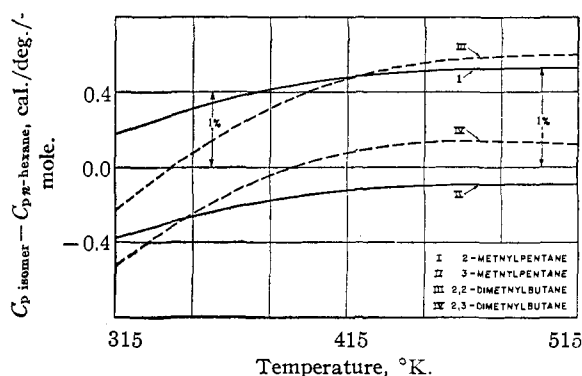


Fig. 1.—Differences between heat capacity of *n*-hexane and its isomers as a function of temperature.

derived from thermal and vapor-pressure data give an accurate and convenient method of determining volumes and related properties within the temperature and pressure range prescribed by their experimental bases.

**Entropies.**—The entropies of gaseous 2-methylpentane and 2,3-dimethylbutane at 298.16°K. have been computed by Pitzer and Kilpatrick.<sup>10</sup> The heat of vaporization and second virial coefficient data of this paper made it possible to calculate the entropies at other temperatures up to the normal boiling point and to refine the values at 298.16° K. by taking account of gas imperfection. These entropy calculations are summarized in Table VII. The values for the entropy of the liquids are from the work of Douslin and Huffman<sup>15</sup>; at the two higher temperatures moderate extrapolations of the heat-capacity curves for the liquids were required. The vapor-pressure equations of ref. 12 were used.

Since 3-methylpentane has never been frozen, the entropy of the liquid has not been obtained from low-temperature studies. For this compound, values for the entropy of vaporization to the ideal gas at atmospheric pressure were computed, and these calculations are included in Table VII.

**Acknowledgments.**—We wish to thank Mr. J. W. Tooke of the Phillips Petroleum Company for help in obtaining the hydrocarbon samples. We are also indebted to Mr. B. H. Eccleston and Mr. H. J. Coleman for the distillations and purity determinations on the three samples.

(15) Douslin and Huffman, *ibid.*, **68**, 1704 (1946).

TABLE VII

2-Methylpentane			
$T, ^\circ\text{K.}$	298.16	318.2	333.5
$S^\circ, \text{liq.}$	69.45	72.52	74.82
Vaporization, $\Delta H_{\text{vap.}}/T$	23.95	21.58	19.92
Compression, $R \ln (P/760)$	-2.54	-1.02	0.00
Gas imperfection	0.11	0.16	0.22
$S^\circ, \text{gas}$	90.97 $\pm 0.20$	93.24 $\pm 0.20$	94.96 $\pm 0.20$
2,3-Dimethylbutane			
$T, ^\circ\text{K.}$	298.16	313.13	331.15
$S^\circ, \text{liq.}$	66.33	68.57	71.22
Vaporization, $\Delta H_{\text{vap.}}/T$	23.34	21.62	19.69
Compression, $R \ln (P/760)$	-2.34	-1.20	0.00
Gas imperfection	0.10	0.13	0.18
$S^\circ, \text{gas}$	87.43 $\pm 0.20$	89.12 $\pm 0.20$	91.09 $\pm 0.20$
3-Methylpentane			
$T, ^\circ\text{K.}$	298.16	323.8	336.5
Vaporization, $\Delta H_{\text{vap.}}/T$	24.27	21.28	19.95
Compression, $R \ln (P/760)$	-2.76	-0.83	0.00
Gas imperfection	0.07	0.13	0.18
$\Delta S^\circ, \text{liquid to ideal gas at 1 atm.}$	21.58 $\pm 0.05$	20.58 $\pm 0.05$	20.12 $\pm 0.05$

## Summary

The vapor heat capacities of 2-methylpentane, 3-methylpentane and 2,3-dimethylbutane have been measured over the temperature range 325 to 471°K. Values of the heat capacity of the ideal gases are given by the following empirical equations.

2-Methylpentane:

$$C_p^\circ = 1.55 + 0.11963T - 3.478 \times 10^{-5}T^2$$

3-Methylpentane:

$$C_p^\circ = 1.40 + 0.11776T - 3.291 \times 10^{-5}T^2$$

2,3-Dimethylbutane:

$$C_p^\circ = -2.65 + 0.13692T - 5.433 \times 10^{-5}T^2$$

Heats of vaporization for the three compounds were measured at three temperatures ranging from about 25° to the normal boiling point. For interpolation the following equations may be used:

2-Methylpentane:

$$\Delta H_{\text{vap.}} = 9173 - 0.2673T - 0.02196T^2$$

3-Methylpentane:  $\Delta H_{\text{vap.}} = 9688 - 3.366T - 0.01629T^2$

2,3-Dimethylbutane:

$$\Delta H_{\text{vap.}} = 8461 - 2.233T - 0.02438T^2$$

Entropies of 2-methylpentane and 2,3-dimethylbutane in the ideal gas state are given at the normal boiling points, at 298.16°K. and at an intermediate temperature.

Second virial coefficients derived from the thermal data are shown to be consistent with literature data on vapor densities.

BARTLESVILLE, OKLA.

RECEIVED MAY 16, 1949

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

## The Solubility of Cuprous Chloride and Silver Bromate in Aqueous Solutions of Unsaturated Alcohols<sup>1a</sup>

BY R. M. KEEFER, L. J. ANDREWS AND R. E. KEPNER

Extensive information concerning the reactions of allyl alcohol and certain unsaturated acids to form water-soluble complexes with cuprous ion and cuprous chloride has been accumulated.<sup>1b,c,d,e,f</sup>

By solubility measurements of the type used in previous investigations data have now been obtained concerning the tendency for certain allylic alcohols to form cuprous complexes. The equilibrium constants for these metalation reactions are reported here and are compared with those obtained for the unsaturated acids. Measurements of the solubility of silver bromate in aqueous solutions of certain of these alcohols and of a few other compounds of interest are also reported, the results of which may be explained satisfactorily on the assumption that a 1:1 complex between silver

ion and the unsaturate is formed.<sup>2</sup> Thus data are available for a comparison of the relative tendencies for cuprous and silver ions to coordinate with a carbon-carbon double bond.

**The Solubility Measurements.**—The method of determining the solubility of cuprous chloride in aqueous solutions of unsaturated compounds has been described previously.<sup>1d,e,f</sup> All solutions were prepared and saturated with cuprous chloride or silver bromate at 25.0°. For the cuprous chloride series the chloride-ion concentration was varied by addition of hydrochloric acid and the ionic strength maintained at 0.100 by addition of perchloric acid prior to addition of solid cuprous chloride. In the silver bromate experiments potassium nitrate was added to the aqueous solutions of the unsaturated compounds to adjust the ionic strength to 0.10 prior to addition of solid silver bromate. Aliquots of the solutions saturated with silver bromate were analyzed for total silver ion by adding a measured excess of 0.0500 *M*

(1) (a) Cation Complexes of Compounds Containing Carbon-Carbon Double Bonds. V.

(1) (b) Kepner and Andrews, *J. Org. Chem.*, **13**, 208 (1948); (c) Andrews and Keefer, *THIS JOURNAL*, **70**, 3261 (1948); (d) Keefer and Andrews, *ibid.*, **71**, 1723 (1949); (e) Andrews and Keefer, *ibid.*, **71**, 2379 (1949); (f) Keefer, Andrews and Kepner, *ibid.*, **71**, 2381 (1949).

(2) Cf. Winstein and Lucas, *ibid.*, **60**, 836 (1938).