

It is quite clear that the calculated values do not agree at all with those found except in the case of potassium and ammonium formate. This fair agreement in two cases makes the disagreement in the others more striking. If none of the values showed agreement, the disagreement might be explained for the formates by the lack of an accurate value for the migration velocity for formate ion in aqueous solution and in the case of hydrogen chloride by the probable inaccuracy of our value for the formic acid solution (although the inaccuracy could not be nearly large enough to account for the enormous discrepancy in this particular case).¹ Or the disagreement might be explained by saying that the simple viscosity relationship assumed is not correct in any case. But since the relationship gives, in some cases, values which agree and in others values which disagree with the experimental ones, it is clearly shown that the difference in viscosity of the solvents does not affect all ions alike.² It is, therefore, not permissible to set up a general equation expressing a relationship between the conductivities at infinite dilution in various solvents and the viscosities alone.³ In formic acid, for instance, the mobilities of the ions do not seem to differ from each other as much as they do in aqueous solutions.⁴

This work is being continued in this laboratory along the lines indicated in the body of the paper. In addition to the points already mentioned it may be stated that we are repeating some of the measurements at different temperatures from those at which the data herein reported were obtained, and that we are also studying formates of types higher than the uni-univalent ones.

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THE HEAT OF VAPORIZATION OF NORMAL LIQUIDS.

By JAMES KENDALL.

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The theoretical study of the heat of vaporization of liquids—a branch of physical chemistry long neglected—has recently attracted a great deal of investigation. The subject is of interest from its connection with the equation of van der Waals and the problem of molecular attraction. A number of formulas for representing variation of heat of vaporization with temperature have lately been put forward; some of these claim a theoretical basis, some are admittedly empirical. During the past year,

¹ The data for HCl are discussed on p. 1616.

² This may be due to differences in the solvation of the various ions in the two solvents.

³ See Walden, *Z. physik. Chem.*, **55**, 207 (1906) for references.

⁴ See Kraus, *loc. cit.*

in particular, the rate of appearance of new formulas has increased to the proportions of an epidemic.

It has seemed of importance, therefore, to the author, in view of previous work upon the subject, to make a critical examination of the various equations that have been proposed. Their relative theoretical merits—a field already fruitful in polemics—are not touched upon at all in this paper. The sole point of investigation is agreement with the experimental data. In the present imperfect state of our knowledge of this subject, where even first principles are hotly disputed, it appears reasonable to apply to all equations the one practical test, free from any possible bias—the test of accuracy.

It is true that we possess no direct determinations of heats of vaporization for any normal liquid, throughout an extended temperature range, sufficiently trustworthy to be of value for the above purpose. However, the thermodynamical equation of Clausius and Clapeyron (see Equation 1 below) affords a method of obtaining the heat of vaporization indirectly by the measurement of other quantities. These quantities are all accurately determined for a large number of liquids and through a wide range of temperature in the extensive researches of Young and his collaborators.

The results of Young have recently been revised and published in collected form.¹ The necessary data are now available for thirty pure liquids, of which twenty-six are normal or non-associated.

It is impossible, from space considerations, to examine all of those in the present paper; consequently, a few typical cases have been selected. The agreement of the various formulas with the experimental results for octane, methyl butyrate, carbon tetrachloride and fluorobenzene is tested in the tables given below.

The above liquids were chosen, without previous knowledge as to the nature of the results they would supply, for the following reasons. It is important, in testing any function which varies with temperature, to be able to consider as large a temperature range as possible. Hence octane was selected from the ten hydrocarbons investigated by Young, since it possesses the highest critical temperature. (The lowest temperature for which data are available is 0° in all cases.) Methyl butyrate was chosen as the typical example of the ten esters studied, for the same reason. The remaining liquids—carbon tetrachloride and fluorobenzene—are among those regarded by investigators as “characteristically” normal liquids;² both have, also, high critical temperatures. That the data selected are really representative may be confirmed by a study of the collected tables.³

¹ Young, *Proc. Roy. Soc. Dublin*, **12**, 374 (1910).

² Applebey and Chapman, *J. Chem. Soc.*, **105**, 742 (1914).

³ Mills, *THIS JOURNAL*, **31**, 1099 (1909).

The equations examined are developed briefly below: The following notation is employed.

T —absolute temperature	R —constant of gas equation, $PV = RT$, equal, under the units employed, to $62340/M$
t —temperature centigrade	T_c —critical temperature
V —volume of one gram of saturated vapor.	v —volume of one gram of liquid
d —density of liquid	d_c —critical density
D —density of saturated vapor	P —vapor pressure in mm. of mercury
P_c —critical pressure	L —total heat of vaporization ¹ of one gram of liquid, expressed in calories
M —molecular weight	

With this notation, the thermodynamical equation is expressed as follows:

$$L = 0.0431833 (dP/dT)T. (V - v) \quad (1)$$

(The numerical factor is the reciprocal of the value of the mechanical equivalent of heat under the units stated.) The heat of vaporization at any temperature is thus obtained in terms of T , V , v and dP/dT , and the degree of accuracy of the calculated value will depend upon the limits of experimental error in the determination of these quantities, and upon the relative effect of such errors in the calculation of the equation. These points have been carefully examined by Mills.² The conclusion drawn is that, except at zero centigrade and in the neighborhood of the critical temperature, the calculated values for the heat of vaporization are substantially true. At 0° C. the values derived are usually too high; near T_c the difficulty in the exact determination of dP/dT renders the results somewhat uncertain. The above equation may, therefore, be safely employed as a basis for comparison throughout the greater part of the experimental range, small divergences at 0° C. and near T_c being disregarded.

A simple formula developed by Mills:³

$$L = 0.0431833 P (V - v) + \mu'(\sqrt[3]{d} - \sqrt[3]{D}) \quad (2)$$

(μ' is a constant varying with the liquid under consideration) has been thoroughly tested by him, and found to be in excellent agreement throughout with the thermodynamical equation for all normal liquids. For its theoretical significance reference must be made to the original papers.

A third formula, proposed by Dieterici:⁴

$$L = 0.0431833 P (V - v) - 4.577 c (T/M) \log (d/D) \quad (3)$$

(c is a constant varying with the liquid) has also been examined by Mills.² It is found to be consistently inaccurate at low temperatures, although

¹ Internal + external, at constant temperature T .

² Mills, *Loc. cit.*

³ Mills, *J. Phys. Chem.*, **6**, 209 (1902); **8**, 383 and 593 (1904); **9**, 402 (1905); **10**, 1 (1906); **11**, 132 and 594 (1907); **13**, 512 (1909); **15**, 417 (1911); **18**, 101 (1914).

⁴ Dieterici, *Ann. Physik*, **25**, 569 (1908).

the agreement at higher temperatures is remarkably good. A similar equation was previously suggested by Crompton.¹

Kleeman² has deduced mathematically, from assumptions regarding molecular attraction, the equation:

$$L = 0.0431833 P (V - v) - K (d^2 - D^2) \quad (4)$$

(K is a constant varying with the liquid.) The same equation has also been put forward by Batschinski.³

The present author⁴ has shown that the following simple relation holds:

$$L = k(T_c - T)^n \quad (5)$$

(k is a constant varying with the liquid, n is for all normal liquids equal to 0.386.) Later investigation showed that the above is an interpolation formula, and is dependent upon the two equations:

$${}^3\sqrt{d} - {}^3\sqrt{d_c} = k_1(T_c - T)^{1/3}$$

$${}^3\sqrt{d_c} - {}^3\sqrt{D} = k_2(T_c - T)^{1/2}$$

which were demonstrated to hold satisfactorily for normal liquids. By combining these equations with that of Mills (Equation 2 above), we obtain:

$$K = 0.0431833 P (V - v) + k_1\mu'(T_c - T)^{1/3} + k_2\mu'(T_c - T)^{1/2} \quad (5a)$$

This is the more correct expanded form of Equation 5 above. The first part of the equation represents the external heat of vaporization, which is variable in magnitude, but at most temperatures is comparatively small; the exponent $n = 0.386$ in Equation 5 is, consequently, intermediate between the two simple values (one-third and one-half) in Equation 5a. For associated liquids the equation still holds if the value of n is modified.⁵

Tyrer⁶ has recently proposed a somewhat similar formula:

$$L = 0.0431833 P (V - v) + C(T_c - T)^{1/3}/(d^{1/3} + D^{1/3}) \quad (6)$$

C is a constant varying with the liquid under examination.

Applebey and Chapman⁷ have deduced the relation:

$$L = RT \log_e (V - b)/(v - b) + RT^2[1/(v - b) + 1/(V - b)] db/dT \quad (7)$$

¹ Crompton, *Proc. Chem. Soc.*, **17**, 61 (1901).

² Kleeman, *Phil. Mag.*, [6] **20**, 665 (1910). A somewhat different formula was advanced in a previous paper, *Phil. Mag.*, [6] **19**, 795 (1910).

³ Batschinski, *Ann. Physik*, **14**, 288 (1904).

⁴ Kendall, *Meddel. från K. Vet-Akads. Nobelinstitut*, Band **2**, No. 29 (1912); "The Properties of Liquids as Functions of the Critical Constants." Since this paper is not generally available, the significance of the equation is briefly indicated above.

⁵ Kendall, *Meddel. från K. Vet-Akads. Nobelinstitut*, Band **2**, No. 36 (1913); "The Heat of Vaporization of Associated Liquids."

⁶ Tyrer, *J. Phys. Chem.*, **17**, 717 (1913).

⁷ Applebey and Chapman, *J. Chem. Soc.*, **105**, 734 (1914). The equation, in the original paper, is referred to molecular volumes. These are here changed to V and v (volume of 1 g.). The constant b in 7 is consequently the usual van der Waals' constant divided by M (mol. wt.). The same holds for equation 10.

in which b (the constant of van der Waals' equation) is assumed to vary linearly with the temperature. Methods for the determination of b_c (the value of b at the critical temperature) and db/dT are developed; when these quantities are known, L can be evaluated.

Rodzewitz¹ has recently put forward the equation:

$$L = 0.0431833 KT^2 \{ (P_c - P)/P \}. (dP/dT) \quad (8)$$

(K is a constant varying with the liquid.)

The validity of this equation depends on that of the relation:

$$(V - v) = KT(P_c - P)/P$$

On examination, however, it is found that, while the above relation is approximately true at low temperatures (as the figures given by Rodzewitz show), yet it fails entirely at temperatures approaching the critical point. This will be evident from the following tabulation where the results for octane and carbon tetrachloride are shown:

t .	80	100	120	140	160	180	200	220	240	260	280
100 K (CCl ₄) . .	1.16	1.15	1.15	1.16	1.19	1.21	1.26	1.35	1.54	1.99	6.44
100 K (octane)	2.79	2.81	2.83	2.85	2.90	3.04	3.28	3.83	5.52

The equation can, therefore, be employed only at low temperatures. The same is true of the general equation of Arrhenius:²

$$L = A_0 - CT^2 \quad (9)$$

where A_0 and C are constants dependent on the liquid. Similarly, the formula of Bakker:³

$$L = RT \log_e (V - b)/(v - b) \quad (10)$$

although directly deduced from the equation of van der Waals, is not in agreement with the results of experiment. Finally, there may be mentioned the equation of McLewis:⁴

$$L = (T/\alpha)(d/\beta) \quad (11)$$

(α = coefficient of expansion, β = compressibility) which gives approximate agreement with the experimental values for the few cases where data for normal liquids are available.

It will be seen that most of the above equations contain a constant dependent upon the liquid under consideration. It is usually possible to remove this, and so generalize the equation, by combination with the rule of Trouton or some similar law. Thus equation 5 becomes:

$$ML = 20.7 T_c(1 - T/T_c)^n \quad (5b)$$

a relation perfectly general for all normal liquids. Since, however, the rule of Trouton is only approximately correct, such equations will not

¹ Rodzewitz, *J. Russ. Phys. Chem. Soc., Phys.* **45**, 355 (1914).

² Arrhenius, *Meddel från K. Vet.-Akads. Nobelinstitut*, Band 2, No. 8 (1911).

³ Bakker, *Z. Physik. Chem.*, **18**, 519 (1895).

⁴ McLewis, *Phil. Mag.*, [6] **22**, 268 (1911).

usually reproduce the experimental values sufficiently closely to be of practical utility.

In the following tables only those equations (2 to 7, inclusive) are compared with the thermodynamical Equation 1 which are applicable throughout the whole of the available experimental range. The constants employed are shown in Table I; values not tabulated previously, and calculated by the present author, are indicated by a star. The collected results are given in Tables II-V; divergences from the experimental values

TABLE I.—CONSTANTS OF EQUATIONS.

	Octane.	Methyl butyrate.	Carbon tetrachloride.	Fluorobenzene.
T_c	569.2	554.25	556.15	559.55
μ' (Mills).....	93.16	91.31	44.01	85.65
c (Dieterici).....	1.858	1.824	1.667	1.711
K (Kleeman).....	176.2	113.3*	19.74	81.44
k (Kendall).....	9.72	10.47	5.92	10.04
C (Tyrer).....	134.4*	140.8*	133.0*	146.0*
b_c (Applebey).....	190.63	131.74	107.54	105.85
db/dt (Applebey).....	0.11732	0.08459	0.06674	0.06472

TABLE II.—OCTANE. HEATS OF VAPORIZATION.

t .	Ther.	Mills.	Dieterici.	Kleeman.	Kendall.	Tyrer.	Applebey.
0	89.46	85.69	97.63	95.69	87.49	89.83	...
120	71.43	71.83	73.05	73.37	71.56	72.38	73.82
140	68.28	68.61	69.36	69.36	68.28	68.83	...
160	64.75	65.06	65.52	65.31	64.79	64.96	...
180	60.91	61.14	61.40	60.90	60.93	60.85	59.57
200	56.61	56.72	56.89	56.15	56.64	56.38	...
220	52.03	51.80	51.83	50.98	51.81	51.39	...
240	45.97	45.72	45.63	44.76	46.02	45.57	42.92
260	39.14	38.63	38.46	35.75	38.85	38.61	...
280	28.26	28.17	27.85	27.55	28.50	28.69	25.96
290	19.10	19.50	19.12	19.20	19.35	20.34	17.87

TABLE IIa.—OCTANE. DIVERGENCES.

t .	Mills.	Dieterici.	Kleeman.	Kendall.	Tyrer.	Applebey.
0	-3.77	+8.17	+6.23	-1.97	+0.37	...
120	+0.40	+1.62	+1.94	+0.13	+0.95	+2.39
140	+0.33	+1.08	+1.08	0.00	+0.55	...
160	+0.31	+0.77	+0.56	+0.04	+0.21	...
180	+0.23	+0.49	-0.01	+0.02	-0.06	-1.34
200	+0.11	+0.28	-0.46	+0.03	-0.23	...
220	-0.23	-0.20	-1.05	-0.22	-0.64	...
240	-0.25	-0.34	-1.21	-0.05	-0.40	-3.05
260	-0.51	-0.68	-1.39	-0.29	-0.53	...
280	-0.09	-0.41	-0.71	+0.24	+0.43	-2.30
290	+0.40	+0.02	+0.08	+0.25	+1.24	-1.23
Av. (120-280°)	0.27	0.65	0.93	0.11	0.44	2.13

are shown in Tables IIa-Va. In the calculation of the "average divergence," the figures for 0° and for temperatures within 10° of the critical are disregarded.¹

TABLE III.—METHYL BUTYRATE. HEATS OF VAPORIZATION.

<i>t.</i>	Ther.	Mills.	Dieterici.	Kleeman.	Kendall.	Tyrer.	Applebey.
0	95.79	90.91	101.88	101.17	92.35	95.08	...
100	77.80	78.13	79.58	80.41	77.95	79.02	...
120	74.31	74.72	75.58	76.10	74.48	75.17	80.79
140	70.84	71.04	71.61	71.62	70.77	71.13	...
160	66.53	66.87	67.08	66.87	66.69	66.77	65.88
180	62.00	62.26	62.45	61.79	62.26	62.01	...
200	57.41	57.19	57.31	56.43	57.18	56.86	55.20
220	51.31	51.07	51.08	50.23	51.28	50.83	...
240	44.14	43.69	43.61	42.70	44.00	43.74	...
260	34.44	34.06	33.85	33.26	34.10	34.25	32.00
280	11.16	11.98	11.64	12.42	11.59	12.62	11.77

TABLE IIIa.—METHYL BUTYRATE. DIVERGENCES.

<i>t.</i>	Mills.	Dieterici.	Kleeman.	Kendall.	Tyrer.	Applebey.
0	-4.88	+6.09	+5.38	-3.44	-0.71	...
100	+0.33	+1.78	+2.63	+0.15	+1.22	+2.99
120	+0.41	+1.27	+1.89	+0.17	+0.86	...
140	+0.20	+0.77	+0.78	-0.07	+0.29	...
160	+0.34	+0.55	+0.34	+0.16	+0.24	-0.65
180	+0.26	+0.45	-0.21	+0.26	+0.01	...
200	-0.22	-0.10	-0.98	-0.23	-0.55	-2.21
220	-0.24	-0.23	-1.08	-0.03	-0.52	...
240	-0.45	-0.53	-1.44	-0.14	-0.40	...
260	-0.38	-0.59	-1.18	-0.34	-0.19	-2.44
280	+0.82	+0.48	+1.26	+0.43	+1.46	+0.61
Av. (100-260°)	0.31	0.70	1.19	0.17	0.48	2.00

TABLE IV.—CARBON TETRACHLORIDE. HEATS OF VAPORIZATION.

<i>t.</i>	Ther.	Mills.	Dieterici.	Kleeman.	Kendall.	Tyrer.	Applebey.
0	51.87	52.40	54.13	56.14	52.36	53.62	...
80	46.00	46.44	46.11	47.41	46.03	46.60	...
100	44.15	44.58	44.20	45.16	44.23	44.58	44.33
120	42.08	42.54	42.18	42.75	42.30	42.44	...
140	39.92	40.36	40.11	40.35	40.22	40.21	...
160	37.95	38.08	37.99	37.92	37.95	37.86	38.38
180	35.40	35.46	35.47	35.22	35.43	35.25	...
200	32.61	32.52	32.67	32.18	32.62	32.39	...
220	29.45	29.14	29.35	28.77	29.33	29.13	29.72
240	25.56	25.10	25.35	24.76	25.33	25.24	...
260	20.07	19.70	19.89	19.49	19.90	20.05	...
280	10.43	10.45	10.48	10.48	9.22	10.29	10.71

¹ Applebey and Chapman have calculated all results (except for fluorobenzene) at intervals of 30°. In the tables their figures for intermediate temperatures are omitted to economize space, but for the final calculation of "average divergences" all results within the temperature range indicated above have been taken into account.

TABLE IVa.—CARBON TETRACHLORIDE. DIVERGENCES.

<i>t.</i>	Mills.	Dieterici.	Kleeman.	Kendall.	Tyrer.	Applebey.
0	+0.53	+2.26	+4.27	+0.49	+1.75	...
80	+0.44	+0.11	+1.41	+0.03	+0.60	...
100	+0.43	+0.05	+1.01	+0.08	+0.43	+0.18
120	+0.46	+0.10	+0.67	+0.22	+0.36	...
140	+0.44	+0.19	+0.43	+0.30	+0.29	...
160	+0.13	+0.04	-0.03	0.00	-0.09	+0.43
180	+0.06	+0.07	-0.18	+0.03	-0.15	...
200	-0.09	+0.06	-0.43	+0.01	-0.22	...
220	-0.31	-0.10	-0.68	-0.12	-0.32	+0.27
240	-0.46	-0.21	-0.80	-0.23	-0.32	...
260	-0.37	-0.18	-0.58	-0.17	-0.02	...
280	+0.02	+0.05	+0.05	-1.21	-0.14	+0.28
Av. (80-260°)	0.32	0.11	0.62	0.12	0.28	0.28

TABLE V.—FLUOROBENZENE. HEATS OF VAPORIZATION.

<i>t.</i>	Ther.	Mills.	Dieterici.	Kleeman.	Kendall.	Tyrer.	Applebey.
0	87.78	88.39	93.51	94.80	89.14	91.44	...
80	80.07	79.11	79.53	80.56	78.60	79.99	79.76
100	77.10	76.11	76.19	76.79	75.59	76.48	77.21
120	73.03	72.69	72.55	72.80	72.34	72.80	73.24
140	68.75	69.00	68.79	68.71	68.84	68.91	69.27
160	64.37	64.99	64.79	64.45	64.97	64.81	65.39
180	60.17	60.65	60.55	59.91	60.87	60.41	61.08
200	55.35	55.79	55.78	54.91	56.16	55.63	55.84
220	50.37	50.36	50.51	49.41	50.73	50.27	50.34
240	44.07	43.80	43.97	43.00	44.22	43.87	43.77
260	35.65	35.32	35.43	34.70	35.60	35.64	35.21
280	20.82	21.16	21.07	20.17	20.74	21.60	19.95

TABLE Va.—DIVERGENCES.

<i>t.</i>	Mills.	Dieterici.	Kleeman.	Kendall.	Tyrer.	Applebey.
0	+0.61	+5.73	+7.02	+1.36	+3.66	...
80	-0.96	-0.54	+0.49	-1.47	-0.08	-0.31
100	-0.99	-0.91	-0.31	-1.51	-0.62	+0.11
120	-0.34	-0.48	-0.23	-0.69	-0.23	+0.21
140	+0.25	+0.04	-0.04	+0.09	+0.16	+0.52
160	+0.62	+0.42	+0.08	+0.60	+0.44	+1.02
180	+0.48	+0.38	-0.26	+0.70	+0.24	+0.91
200	+0.44	+0.43	-0.44	+0.81	+0.28	+0.49
220	-0.01	+0.14	-0.96	+0.36	-0.10	-0.03
240	-0.27	-0.10	-1.07	+0.15	-0.20	-0.30
260	-0.33	-0.22	-0.95	-0.05	-0.01	-0.44
280	+0.34	+0.25	-0.65	-0.08	+0.78	-0.87
Av. (80-260°)	0.47	0.37	0.48	0.64	0.24	0.43

In the discussion of the above figures, Tables II-IV will be considered first, since the results obtained are essentially the same throughout.

Table V (fluorobenzene) gives results of a different nature, requiring further investigation; it is, therefore, dealt with subsequently.

From the results obtained with octane, methyl butyrate and carbon tetrachloride, it is evident that the equations of Kendall and of Mills afford values most consistent with the experimental figures. The divergences are always small, except at 0° and near the critical point, where the experimental values are liable to error. Even at these temperatures the divergences are usually smaller than those obtained with the remaining formulas. The equations of Kleeman and of Dieterici (and, to a smaller degree, that of Tyrer) are not so accurate, and lead to values at the lowest temperatures which are consistently too high. The equation of Applebey and Chapman gives values differing fairly considerably from the experimental. It must be mentioned, however, that the effect of small experimental errors upon the calculated values is much greater here than in any of the other equations.

The final table for fluorobenzene shows exactly the opposite results. The equations of Kendall and of Mills here give the poorest agreement with the experimental data. (Kleeman's values may be appreciably improved by a slight modification in the value of the constant employed by him.) Also, for practically all of the formulas, the calculated values at the lowest temperatures (80 – 120°) are uniformly too low.

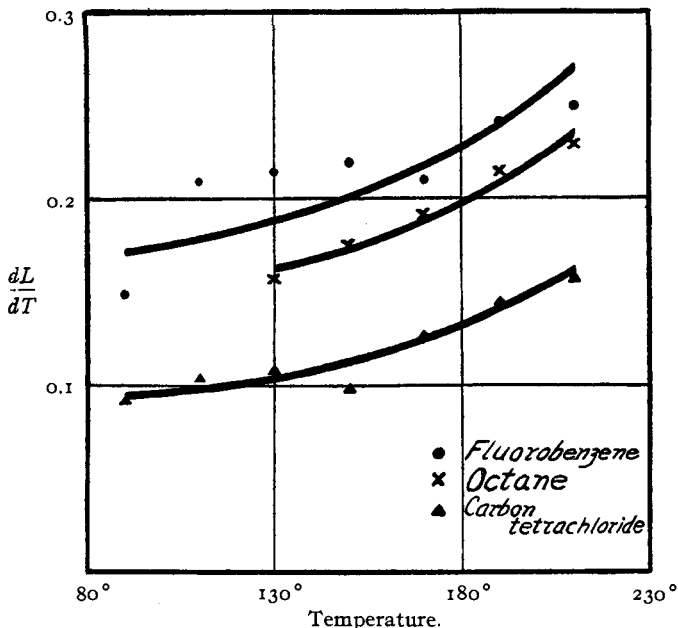
This difference in behavior may be satisfactorily explained by a consideration of the experimental data. It is found on examination that the values for fluorobenzene at low temperatures are affected by errors of observation.

The method employed for illustrating this is as follows: The function dL/dT is plotted against temperature. Now, in all normal curves, the heat of vaporization, after a rapid increase with decreasing temperature near the critical point, increases more and more slowly as temperature is further lowered. When the rate of this increase (dL/dT) is plotted against T , therefore, we obtain a smooth curve, with rapid change of slope near the critical temperature, but approximating more nearly to a straight line at lower temperatures. The values for dL/dT will decrease continuously, but more and more slowly, as temperature falls.

The results for the lower temperatures are shown in the accompanying diagram. The values for dL/dT are found, at intervals of 20° , by interpolation from the preceding tables, *e. g.*, for octane at 130° , $dL/dT = 1/20 (L_{120} - L_{140})$. It is evident that, while the results for octane and carbon tetrachloride lie fairly closely upon smooth curves of the required type, the values obtained in the case of fluorobenzene show considerable fluctuations.¹ The experimental data in this case are clearly inconsistent,

¹ The values for methyl butyrate are not plotted to avoid confusion in the diagram. The curve is almost identical with that for fluorobenzene. The agreement in this case is not quite so good as with octane or carbon tetrachloride.

and a repetition of the observations would probably lead to results in agreement with those obtained from other liquids, *i. e.*, exhibiting close concordance with Equations 2 and 5.



It is in this direction—the correction of the experimental data—that the equation of Mills has already repeatedly proved itself to be of service. Large divergences were existent between the original experimental values of Young and the calculated values of Mills for several liquids. It was invariably found, when the observations were repeated, that the *experimental values* were in error.¹

The utility of the various equations proposed will probably be restricted, for the present, to this practical application. It is hard to conceive how much progress can be made on the theoretical side until the fundamental points at issue are settled. For the most obvious conclusion to be drawn from the present investigation is that the heat of vaporization is a quantity which is peculiarly adaptable to representation by empirical formulas. It is impossible that all of the equations considered can be of theoretical significance. Were this the case, an army of physicists might devote their lives to tabulating the different relations, between the quantities concerned, obtainable by the combination and recombination of these equations.² It will be evident, however, that the fact that a formula,

¹ Mills, *Phil. Mag.*, [6] 21, 84 (1911); 24, 483 (1912).

² From three equations alone, Mills obtained thirty-six new relations (*THIS JOURNAL* 31, 1099 (1909)). The number possible soon increases to billions as more equations are introduced. (Compare Bridgman. *Phys. Rev.* 2, 272 (1914).)

in this field, fits the experimental results is no confirmation, taken alone, of the truth of the principles involved.

Further approximate or empirical relations will consequently be superfluous, so long as the fundamental theoretical principles of the subject remain indefinitely outlined. The rigorous mathematical development of the laws of molecular attraction—a field in which Mills has already performed valuable pioneer work—is the necessary prerequisite to any real progress.

Summary.

The accuracy of the various equations proposed for representing heats of vaporization has been tested by comparison with the experimental data of Young. In three out of the four cases examined, the equations of the author and of Mills afford most satisfactory agreement. In the remaining case the experimental figures are shown to be inaccurate.

It has been pointed out that the heat of vaporization is a quantity so adapted to representation by different formulas that no conclusions can be drawn as to their relative theoretical merits. At present, the equations are useful only as checks upon the experimental data.

NICHOLS LABORATORIES OF INORGANIC CHEMISTRY,
COLUMBIA UNIVERSITY, NEW YORK CITY.

THE POTENTIAL OF SILVER IN NONAQUEOUS SOLUTIONS OF SILVER NITRATE.¹

BY VERNETTE L. GIBBONS AND F. H. GETMAN.

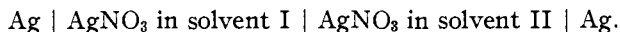
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1. Introduction: (a) Aim of the Investigation; (b) Preparation of Materials. 2. Measurements of Electrical Conductance. 3. Determination of Transport Numbers. 4. Determination of the Electromotive Force of Various Concentration Cells. 5. Discussion of Results. 6. Summary. 7. Chronological Bibliography.

1. Introduction.

The study of the potentials of metals in nonaqueous solutions of their salts was begun by Campetti² about twenty years ago. Since, however, the drop electrode was employed in these experiments the results cannot be considered trustworthy.

A few months later, Jones³ published results of measurements of the combinations



The solvents used were water, ethyl alcohol, methyl alcohol and acetone.

¹ A Dissertation presented to the Faculty of Bryn Mawr College by Vernetta L. Gibbons in part fulfilment of the requirements for the degree of Doctor of Philosophy.

² *Atti accad. Torino*, **28**, 61 and 228 (1893).

³ *Z. physik. Chem.*, **14**, 346 (1894).