$$\log \frac{\pi}{p} = 1.75 \log \frac{\tau}{T} + \alpha' \left[\left(\frac{\tau}{T} - 1 \right) - \frac{1}{2.36} \left(1 - \frac{T}{\tau} \right) \right]$$

was found to agree satisfactorily with the results of observation. The values of α' have been determined for as many substances as possible. The values are found to increase quite regularly in proportion to the complexity of the molecule, being smallest for hydrogen and the monatomic gases and greatest for the associated alcohols of high molecular weight. It has been shown that these values may be represented by an equation

$$M\alpha' = 42l + 1.9m + 41n + \dots$$

where M is the molecular weight of the substance and $l, m, n, \dots$ are the number of atoms of the elements, carbon, hydrogen, oxygen, $\dots$ respectively in the molecule.

BERLIN, March, 1906.

THE RELATION OF HEAT OF VAPORIZATION TO BOILING-POINT.

BY EUGENE C. BINGHAM.

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TROUTON'S rule states that the quotient of the molecular heat of vaporization divided by the absolute temperature of the boiling-point is a constant. This has been accepted as approximately true for normal substances. Acetic acid, however, gives an abnormally small value, which is accounted for by van't Hoff¹ by the fact that the molecules of acetic acid are largely associated both in the liquid and vapor, which would cause the true molecular heat of vaporization to be much larger than the one found. In the case of ethyl alcohol, the vapor is normal but the liquid is associated, so the breaking down of association being connected with an absorption of heat accounts for the abnormally high value of this substance.

More recently Nernst² has pointed out that even among unassociated compounds, the values of this quotient increase considerably with the temperature, if we only choose substances boiling at widely different temperatures. Nernst gave, as a closer approximation to the true values, the equation:

$$\frac{\lambda'}{T_0} = 8.5 \log T_0,$$

¹ Theor. Chemie, Vol. III, p. 54, 2d ed.

² Nachrichten Kgl. Ges. Wiss. Göttingen, 1906.

where T_0 is the boiling-point and λ' the molecular heat of vaporization.

This approximation is shown by the following table taken from Nernst's paper:¹

TABLE I.

Substance.	λ		T_0 .	λ' calc.	λ' obs.	$\frac{\lambda'}{T_0}$	$8.5 \log T_0$.
	$\frac{T_1+T_2}{2}$	$1 - \frac{p}{\pi}$					
Hydrogen.....	20.4	229					
Hydrogen.....	18.1	234	20.4	213		10.4	11.1
Nitrogen.....	76.7	1428					
Nitrogen.....	73.9	1446	77.5	1386	1334	17.9	16.1
Argon.....	87.1	1445	87	1418		16.3	16.5
Oxygen.....	90.1	1692					
Oxygen.....	83.6	1719	90.6	1660	1629	18.3	16.7
Hydrochloric acid.....	190	3542	190	3500		18.4	19.4
Hydrogen sulphide...	213	4620	213	4580		21.5	19.8
Carbon disulphide....	273	6766					
Carbon disulphide....	318	6580	319	6490	6384	20.4	21.2
Ether.....	273	7088					
Ether.....	308	6626	307	6440	6660	21.0	21.3
Benzene.....	353	7640	353	7490	7254	21.2	21.7
Propyl acetate.....	373	8570	375	8310	8000	22.2	21.8
Aniline.....	455	10740	457	10540		23.1	22.6

Following Prof. Nernst's suggestion, I have examined a large number of substances in order to throw light on this relation, and if possible to derive a more accurate one. I have calculated the heat of vaporization by means of a formula devised by Nernst,¹

$$\frac{\lambda}{1 - \frac{p}{\pi}} = R \frac{T_1 T_2}{T_1 - T_2} \ln \frac{p_1}{p_2},$$

where R is the gas constant, π the critical pressure, and p , p_1 , p_2 , the vapor-pressures at the temperatures T , T_1 , T_2 , respectively, and where T_1 and T_2 are taken near enough together so that their arithmetical and geometrical means are practically identical. As is seen in the following tables, the values thus calculated for λ' are in very satisfactory agreement with those obtained by direct observation and given under λ' obs. Only in a few cases marked with a * are the values of λ' uncertain, as shown by the irregularity of the temperature coefficients as calculated. In a few cases marked by a † it was necessary to estimate the critical pressure

¹ Loc. cit.

TABLE II.¹

TABLE II—Continued.

Substance.	$\frac{T_1 + T_2}{2}$	λ $\frac{p}{1 - p}$	π atm.	T_0	λ' calc.	λ' obs.	$\frac{\lambda'}{T_0}$	$8.5 \log T_0$	$17 + 0.011 T_0$	Diff.
Toluene	367.5	8826	41.6	383.8	8155	7695	21.3	22.0	21.2	0.1
Toluene	377.9	8355								
Stannic chloride.....	376.6	8540	36.95	386.9	8221	7962	21.2	22.0	21.3	— 0.1
Stannic chloride	392.2	8403	24.70	398	8594	809*	21.6	22.1	21.4	0.2
Octane	398	8964								
Phenyl chloride.....	408	8592	44.62	405	8482		20.9	22.1	21.5	— 0.6
Phenyl chloride.....	398	8875								
Phenyl bromide.....	423	9367	44.62	428	9121		21.3	22.4	21.7	— 0.4
Phenyl bromide.....	433	9293								
Dimethylorthotoluidine.....	454	10470	30.8	454	10130	9490	22.1	22.6	22.0	0.1
Aniline.....	439.5	11330	52.35	457	10500		23.0	22.6	22.0	1.0
Aniline.....	450.9	10900								
Phenyl iodide.....	398	10682								
Phenyl iodide.....	458	10054	42.62	461.4	9726		20.2	22.6	22.1	— 1.9
Diethylaniline	483.8	11590								
Diethylaniline	471.7	12384	†31.0	488.5	10900		22.2	22.9	22.4	— 0.2
Chloraniline.....	490	12175	†27.0	501.5	11700		23.3	23.0	22.5	0.8
Chloraniline.....	496.7	12220								
p-Nitrotoluene	491.5	12150	†26.6	510.7	11500		22.6	23.0	22.6	0.0
p-Nitrotoluene	504.2	12680								
Chloronaphthalene.....	518.6	11940	†30.2	532.3	11600		21.8	23.0	22.8	— 1.0
Chloronaphthalene.....	522.9	12120								
Bromnaphthalene.....	548.4	12520	†28.9	554.1	12000		21.6	23.3	23.1	— 1.5
Bromnaphthalene.....	544.5	12600								

by means of the calculated value of α' and equation (2) of the preceding paper. The error is not great as the critical pressure only enters in as part of a correction term.

It is observed that the values of "Trouton's constant," in the column $\frac{\lambda'}{T_0}$, increase quite regularly with the temperature among all of the unassociated substances, given under Table II. With the exception of hydrogen and a few other substances, for which the values are uncertain, the values of $\frac{\lambda'}{T_0}$ increase as a linear function of the temperature, and are expressed quite exactly by the equation

$$\frac{\lambda'}{T_0} = 17 + 0.011T_0.$$

The earlier expression

$$\frac{\lambda'}{T_0} = 8.5 \log T_0$$

includes hydrogen but the agreement in general is less satisfactory, as is shown by this more extended study.

The values of $\frac{\lambda'}{T_0}$ for the low boiling esters as shown in Table III are higher than we should expect, as though they were associated, while the higher boiling esters have a normal value, the value of $\frac{\lambda'}{T_0}$ for all of these esters being quite constant at 22.3.

For the associated compounds given in Table IV the values of $\frac{\lambda'}{T_0}$ are considerably larger than the normal value $17 + 0.011T_0$. Hence the difference between these two quantities gives a measure of the association. The differences, *i. e.*, the values of $\frac{\lambda'}{T_0} - (17 + 0.011T_0)$, are given in the last column of the tables. With the alcohols, Table IV, there is practically the same difference in the case of all of the members, indicating that they have equal association. Water, the acids and especially nitric oxide are seen to be highly associated.

CONCLUSIONS.

In this paper a large number of heats of vaporization have been calculated by means of Nernst's formula and found to be in good agreement with observed values.

It has been shown that the values of "Trouton's constant" increase quite regularly and according to the equation

$$\frac{\lambda'}{T_0} = 17 + 0.011T.$$

The divergences in the case of the associated liquids have been considered to be a measure of the association.

In connection with this paper and the preceding one, I wish to express my very sincere appreciation to Prof. W. Nernst for continued counsel and advice.

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THE FREE ENERGY OF SOME HALOGEN AND OXYGEN COMPOUNDS COMPUTED FROM THE RESULTS OF POTENTIAL MEASUREMENTS.

BY M. DE K. THOMPSON.

Received March 23, 1906.

I. INTRODUCTION.

ONE of the most important chemical problems of the present time is the determination of the free energy of formation of compounds from their constituents, for it is this quantity and not the heat evolved that is the true measure of chemical affinity. No reaction can take place of itself that is not capable of doing external work, and the maximum amount of such work which a reaction can produce at any constant temperature is called the free-energy decrease of the reacting system. Although this is a vastly more important quantity than the heat evolved by the reaction, it is one which is known in few cases, compared with those for which the heat-effect has been measured. This is partly due to the greater difficulty of determining the value of the free-energy change, and partly to the fact that its importance has not until recently been generally appreciated. Just as in thermochemical investigations, so here the most fundamental data are the (free)-energy changes attending the formation of various chemical compounds out of their elements; for from these data the free-energy change attending any reaction can be calculated by direct summation.

One method of measuring the free-energy change of a chemical reaction is to determine the conditions of its equilibrium. For a reaction of the general type $aA + bB \dots = eE + fF \dots$ the