

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

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.

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THE RELATION OF HEAT OF VAPORIZATION TO BOILING-POINT.

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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 un-associated 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

Substance.	$\frac{T_1 + T_2}{2}$	$\frac{\lambda}{1 - \frac{\rho}{\pi}}$	π atm.	T_0	λ' calc.	λ' obs.	$\frac{\lambda'}{T_0}$	$\frac{\lambda'}{T_0}$ obs.	8.5 log T_0 .	17+0.011 T.	Diff.
Hydrogen	20.5	225.97									
Hydrogen	20.27	221.33	14.2	20.4	204	10.0	11.1	17.2	— 7.2
Nitrogen	75.4	144.2									
Nitrogen	79.5	134.5	27.5	77.51	1362	1334	17.6	17.2	16.1	17.8	— 0.2
*Carbon monoxide.....	87.3	170.3									
*Carbon monoxide.....	99.8	969	35.5	83.0	1896	18.1	16.5	17.9	0.2
Argon.....	86.33	1478									
Argon.....	87.02	1450	52.9	86.0	1460	17.0	16.4	18.0	— 1.0
Oxygen	89.35	1700									
Oxygen	81.83	1735	50.8	90.6	1664	1629	18.3	18.0	16.7	18.0	0.3
Methane	107.6	1994									
Methane	114.7	1959.6	55.2	108.3	1951	18.0	17.3	18.2	— 0.2
Krypton.....	121.6	2315									
Krypton.....	113	3085	54.3	121.3	2270	18.7	17.7	18.3	0.4
Xenon.....	163.9	3020	57.2	163.9	2970	18.1	18.8	18.8	— 0.7
*Hydrochloric acid.....	190	3542	86.0	190	3500	18.4	19.4	19.1	— 0.7
*Hydrogen sulphide.....	213	4620	92.0	213	4580	21.5	19.8	19.3	2.2
*Hydrogen selenide.....	231	4608	91.0	231	4562	19.8	20.1	19.5	0.3
						$T_1 = 284$					
*Ammonia	236	3923	107.6	236	3960	4950	17.0	17.4	20.2	19.6	— 2.6
*Propane.....	241	3514									
*Propane.....	261	4043	44	236	4000	17.0	20.2	19.6	— 2.6
Ether	308	6643									
Ether	297	6744	35.61	307	6466	6660	21.1	21.7	21.2	20.4	0.7

TABLE II—Continued.

Substance.	$\frac{T_1 + T_2}{2}$	λ												
		$1 - \frac{p}{\pi}$	π atm.	T_0 .	λ' calc.	λ' obs.	$\frac{\lambda'}{T_0}$	$\frac{\lambda'}{T_0}$ obs.	$8.5 \log T_0$.	$17 + 0.011 T$.	Diff.			
Pentane	308	6739												
Pentane	298	6612	33.03	309.5	6469	20.9	21.2	20.4			0.5	
Carbon disulphide	318	6598												
Carbon disulphide	328	6561	77.8	319	6490	6384	20.4	20.0	21.3	20.5			— 0.1	
Acetone	338	6836												
Acetone	328	6988	60.0	329.5	6850	7266	20.8	22.0	21.4	20.6			0.2	
Diisopropyl.....	318	7067												
Diisopropyl.....	328	6895	30.72	331	6627	20.0	21.4	20.6			— 0.6	
Chloroform.....	333	7351												
Chloroform.....	338	7147	54.9	334	7177	6984	21.5	20.9	21.5	20.7			0.8	
Hexane.....	343	7358												
Hexane.....	338	7486	29.62	342	7140	6838	20.9	20.0	21.5	20.8			0.1	
Carbon tetrachloride.....	338	7458												
Carbon tetrachloride.....	348	7368	44.97	349.7	7190	7130	20.6	20.4	21.6	20.8			— 0.2	
Benzene.....	353	7665												
Benzene.....	363	7410	47.89	353.4	7497	7254	21.2	20.5	21.7	20.9			0.3	
Hexamethylene.....	348	7600												
Hexamethylene.....	358	7429	39.82	353.7	7314	7342	20.7	20.8	21.7	20.9			— 0.2	
Phenyl fluoride.....	353	7974												
Phenyl fluoride.....	363	7838	44.62	358.3	7548	21.1	21.7	20.9			0.2	
Heptane.....	368	8099												
Heptane.....	373	7965	26.86	371	7720	7407	20.8	20.0	21.8	21.1			— 0.3	
Diisobutyl.....	378	8380												
Diisobutyl.....	388	8149	24.55	381.5	7962	20.9	21.9	21.2			— 0.3	

TABLE II—Continued.

Substance.	$\frac{T_1 + T_2}{2}$	$\frac{\lambda}{1 - \frac{p}{\pi}}$	π atm.	T_0 .	λ' calc.	λ' obs.	$\frac{\lambda'}{T_0}$	$\frac{\lambda'}{T_0}$ obs.	$8.5 \log T_0$.	$17 + 0.011 T_0$.	Diff.
Toluene	367.5	8826									
Toluene	377.9	8355	41.6	383.8	8155	7695	21.3	20.0	22.0	21.2	0.1
Stannic chloride.....	376.6	8540									
Stannic chloride	392.2	8403	36.95	386.9	8221	7962	21.2	20.6	22.0	21.3	— 0.1
Octane	398	8964	24.70	398	8594	8098	21.6	20.3	22.1	21.4	0.2
Phenyl chloride.....	408	8592									
Phenyl chloride.....	398	8875	44.62	405	8482	20.9	22.1	21.5	— 0.6
Phenyl bromide.....	423	9367									
Phenyl bromide.....	433	9293	44.62	428	9121	21.3	22.4	21.7	— 0.4
Dimethylorthotoluidine.....	454	10470									
Aniline.....	439.5	11330	30.8	454	10130	9490	22.1	20.7	22.6	22.0	0.1
Aniline.....	450.9	10900	52.35	457	10500	23.0	22.6	22.0	1.0
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									
Chloraniline	496.7	12220	†27.0	501.5	11700	23.3	23.0	22.5	0.8
<i>p</i> -Nitrotoluene	491.5	12150									
<i>p</i> -Nitrotoluene	504.2	12680	†26.6	510.7	11500	22.6	23.0	22.6	0.0
Chlornaphthalene.....	518.6	11940									
Chlornaphthalene.....	522.9	12120	†30.2	532.3	11600	21.8	23.0	22.8	— 1.0
Bromnaphthalene.....	548.4	12520									
Bromnaphthalene.....	544.5	12600	†28.9	554.1	12000	21.6	23.3	23.1	— 1.5

TABLE IV.

Substance.	$\frac{T_1 + T_2}{2}$	$\frac{\lambda}{1 - \frac{\rho}{\pi}}$	π atm.	T_0 .	λ' calc.	λ' obs.	$\frac{\lambda'}{T_0}$	$\frac{\lambda'}{T_0}$ obs.	$8.5 \log T_0$.	$17 + 0.011 T$.	Diff.
Nitric oxide.....	113	3085									
Nitric oxide.....	127.5	3625	71.2	123.1	3412	27.7	17.8	18.4	9.3
Chlorine.....	238	5496									
Chlorine.....	248	5243	93.5	239.4	5402	22.5	20.2	19.5	3.0
Bromine.....	328	7450	25.0	328	7200	7292	22.0	22.2	21.4	20.6	1.4
Methyl alcohol.....	338	8947									
Methyl alcohol.....	348	8896	78.63	339	8828	8390	26.0	24.7	21.5	20.7	5.3
Ethyl alcohol.....	338	10400									
Ethyl alcohol.....	348	9785	62.76	351.4	9448	9443	26.9	26.9	21.6	20.9	6.0
Propyl alcohol.....	378	10170									
Propyl alcohol.....	358	10250	50.16	350	10000	10000	27.0	27.0	21.8	21.1	5.9
Water.....	373	9889	194.6	373	9839	9650	26.4	25.9	21.8	21.1	5.3
Formic acid.....	358	8503									
Formic acid.....	368	8398	37.2	373	8180	21.9	21.8	21.1	0.8
Isobutyl alcohol.....	378	10700									
Isobutyl alcohol.....	388	10370	48.27	381	10380	10250	27.2	26.9	21.9	21.2	6.0
Acetic acid.....	388	9340									
Acetic acid.....	393	9349	57.11	391	9180	5094	23.5	12.7	22.0	21.3	2.2
Amyl alcohol.....	388	11385									
Amyl alcohol.....	398	11210	†139	404	11080	27.4	22.1	21.5	5.9
Benzoic acid.....	514.4	14510									
Benzoic acid.....	510.7	14800	†28.9	522	14000	26.8	23.1	22.7	4.1
Mercury.....	628	13800									
Mercury.....	638	13750	†24.6	631	13300	13560	21.1	21.5	23.8	23.9	— 2.8
Sulphur.....	718	16643									
Sulphur.....	728	16595	†19.1	728	16650	23160	22.7	39.3	24.3	25.0	— 2.3

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.

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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