

ART. XXX.—*On Some Relations between Temperature, Pressure, and Latent Heat of Vaporization*; by C. E. LINEBARGER.

THE well-known equation

$$\frac{dp}{dT} = A \frac{\rho}{T(v-v')}, \text{ or } \frac{dp}{dT} = A \frac{\rho}{T dv}, \quad (1)$$

in which p is the pressure; T , the temperature; ρ , the latent heat of vaporization; v , the volume of the saturated vapor; and v' , that of the liquid, may be considered to resume most of the relations between temperature, pressure, and latent heat of vaporization; it expresses fundamental relationships between heat,—and volume-energy, as is at once seen, when it is thrown into the form:

$$dp \, dv = A \rho \frac{dT}{T}, \quad (2)$$

an equation of which the left-hand member contains only the factors of volume-energy, and the right-hand member only those of heat-energy. But certain relationships between these factors of energy were found out quite independently of the fundamental equation; guided by no theoretical considerations, their discoverers, by scrutinizing experimental data, saw some regularities which, when generalized, became laws, although approximate and containing inexplicable anomalies. Also, the

differential forms of equations (1) and (2) do not readily permit of direct comparison with empirical facts; they must first by suitable hypotheses and integrations be thrown into other forms. The comparison of the deductions and discovered relationships with the experimental data generally shows a close correspondence. Sometimes, however, variations and exceptions occur which cannot be referred to experimental errors.

The object of this paper is to give an account of the efforts that have been made and the results that have been obtained in regard to the relations between pressure, temperature, and latent heat of vaporization; to subject to a critical revision all experimental data bearing upon the question; to discuss the differences seemingly present between theory and experiment; and to apply the results to certain practical problems. The division of the matter is the following: first, a historical account of such papers as have dealt with the theoretical side of the question; second, a review in tabular form of experimental data together with a discussion of their comparative value; third, a comparison of the results of theory and experiment; fourth, an application of results to a practical problem.

I.

The first paper in which an endeavor was made to find out relations between latent heats of vaporization and other energy-factors is due to Ure;* this pioneer in this field of research determined the heats of vaporization of a number of common liquids, and concluded from his results that under the same pressure the latent heat of vaporization is inversely proportional to the vapor density.

Desprets,† in a paper read before the French Academy towards the end of the year 1818, but of which merely an abstract seems ever to have been published, communicated the results of some determinations of the latent heats of vaporization of water, alcohol, ether, and essence of terebinthine. An inspection of his data led him to state that a liquid at its point of ebullition requires for volatilization so much the less heat, the denser its vapor; latent heats of vaporization are approximately proportional to densities at the boiling points.

Person‡ after determining the latent heats of vaporization of ten additional liquids, notwithstanding that his results were not as accurate as those of Desprets, as he himself admits, and without giving any data, formulated a law, which is “for the heat of vaporization what the law of Dulong and Petit is for the specific heat,” and “even more general, since it applies to

* Phil. Mag. liii, 191, 1819.

† Ann. Chim. et Phys., xxiv, 323, 1823.

‡ Comptes Rend., xvii, 498, 1843.

simple and to compound bodies without distinction." This law is: "The heats of vaporization of different substances range themselves exactly in the order of their temperatures of ebullition, when, instead of equal weights, atomic weights are taken. In a "Note" three years later Person* reverts to his law, and drawing up a table of latent heats of vaporization from the data due to Favre and Silbermann shows how well his previous statements are corroborated by these determinations. The exceptions presented by the acids are explained away by making allowance for their abnormal vapor densities. In this paper, he puts his law in a somewhat different form: "The amount of heat needed to vaporize substances under the same pressure is identical, when the volume produced is the same, and it is smaller or greater according as the volume produced is smaller or greater."

Trouton† "on comparing the quantities of heat necessary to evaporate at constant pressure quantities of different liquids taken in the ratio of the molecular weights,"—found that the amount of heat required by any body is approximately proportional to its absolute temperature at the point of ebullition." He then propounded the following law: "The molecules of chemically related bodies, in changing from the gaseous to the liquid state at the same pressure, disengage quantities of heat, which may be called the molecular latent heat, directly proportional to the absolute temperature of the point of ebullition."

The above laws are purely empirical; they were found through observation of rows of figures; they have no theoretical grounding; being subject to exceptions and irregularities, they can never as deduced rise to the rank of great generalizations; they have been drawn up by the inspection of experimental data, which is an inversion of the usual order of discovery, experimental data as a rule being a means of corroboration rather than of deduction of laws of nature.

We now pass to the consideration of the work that has been done along theoretical lines in the finding out of relations between heat of vaporization, temperature, and pressure.

The first effort made in this direction is due to Raoul Pictet, in a paper truly remarkable for its time, although it seems to have attracted but little attention. Pictet considers a cycle in which a liquid is evaporated from one chamber, condensed in another, and finally returned to the first. Admitting the validity for the case in hand of the laws of Boyle and Gay-Lussac, he then finds mathematical expressions for the work done and the heat absorbed. In order to equate these essen-

* Comptes Rend., xxiii, 524, 1846.

† Phil. Mag., V., xviii, 54, 1884.

tially independent expressions he makes two hypotheses: 1, the cohesion of liquids is the same for all: 2, Carnot's cycle is applicable to volatile liquids, and to their changes of volume: and there exists a relation between heat taken in and work performed. The expressions finally arrived at show a satisfactory correspondence for the most part with the determinations of latent heats of vaporization made by Regnault. The conclusions which have a bearing upon our subject are: I—The product of the latent heats of liquids at the same pressure by their atomic weights, divided by the absolute temperature at which the vaporization takes place, is the same for all: II—The difference between the internal heats of vaporization at any two temperatures, multiplied by the atomic weights, is a constant number for all liquids.

We will not enter into any discussion of these results, contenting ourselves with remarking that the first conclusion is a plain enunciation of "Trouton's law" mentioned above. If priority of publication has any moment in the choice of the name of a discovery, the law in question ought to be called Pictet's law since the date of Pictet's paper is 1876 and that of Trouton's 1884.

Equation (1) seems first to have been made use of by van der Waals* for the establishing of relationships between temperature, pressure, and latent heat of evaporation. If for p , T , and v , ϵp , $m T$, and $\varphi(m) \frac{b}{v}$ (p , being the critical pressure, T , the critical temperature, b , the covolume, and ϵ , m , $\varphi(m)$, coefficients) be substituted in equation (1), and it be kept in mind that

$$\frac{v\mu}{b} = f(m),$$

(μ being the molecular mass), the equation

$$\frac{d\epsilon}{dm} = \frac{8.273}{A} \cdot \frac{\rho\mu}{T_1} \cdot \frac{1}{\varphi m} \quad (3)$$

or

$$\frac{d\epsilon}{dm} = C \cdot \frac{\rho\mu}{T_1} \cdot \frac{1}{\varphi} \quad (4)$$

results. Now when m is the same, that is, at the same reduced temperature, $\frac{d\epsilon}{dm}$ must have the same value, and as a necessary consequence it follows that

$$\frac{\rho\mu}{T_1} = F(m) \quad (5)$$

* Continuität des gasförmigen und flüssigen Zustandes, p. 137.

where F is a constant number for all bodies. But equation (5) is nothing else than the mathematical expression for "Trouton's law," and again the rightfulness of this name may be justly questioned, for the German translation of van der Waal's book appeared three years before Trouton's paper. Van der Waals called to mind the similarity of the expression as developed just above to the law proposed by Desprets (*loc. cit.*), and drew up a little table of data to see if experiment corroborated theory, which in a certain measure he found to be the case.

Bouty* sought to transform the fundamental equation (1) so as to get the quotient of the molecular heat of vaporization by the square of the absolute temperature equal to a constant. His course of reasoning is as follows. If, in the formula

$$\rho = T(v-v') \frac{dp}{dT} \quad (6)$$

the specific volume of the liquid be neglected in comparison with that of the vapor, and if the density of the latter be normal, it ensues that

$$v = \frac{1}{D\mu} \frac{p_0}{p} \cdot \frac{T}{273}, \quad (7)$$

where D is the absolute specific gravity of hydrogen at the temperature zero and under the pressure of 760^{mm} of mercury. By the combination of (6) and (7) the equation

$$\rho\mu = \frac{p_0}{273D} \frac{T^2}{p} \frac{dp}{dT} \quad (8)$$

is obtained; and if T_0 be the boiling point under the pressure p_0 ,

$$\rho\mu = \frac{T_0^2}{273D} \left(\frac{dp}{dT} \right)_0. \quad (9)$$

If it be admitted with Dalton that all vapors have the same tensions at temperatures equidistant from the boiling points of the liquids which give them off, the expression

$$\left(\frac{dp}{dT} \right)_0$$

must be the same for all liquids, and the expression

$$\frac{\rho\mu}{T_0^2} \quad (10)$$

becomes equal to a constant.

Although Bouty is inclined to admit that Dalton's "law" is incorrect, and hence (10) cannot be constant, he gives a table of "constants" for a number of liquids, of which, as de Heen

* Journ. de Phys., II, iv, 26.

remarks* "it is needless to say that the variations to be found in the values of $\frac{\rho\mu}{T^2}$ are enormous." If, however, it be assumed that $T\frac{dp}{dT}$ be constant,† it at once follows that $\frac{\mu\rho}{T} = \text{constant}$, which is Trouton's or better Pictet's law.

Le Chatelier‡ also has transformed equation (1) into another directly comparable with the results of experiment. After putting it in the form

$$\frac{\rho}{T}dT + A(v-v')dp = 0, \quad (11)$$

(ρ in Le Chatelier's calculations is always taken to be the *molecular* heat of vaporization) by multiplying and dividing the second term by p , he obtained this expression

$$\frac{\rho}{T}dT + Ap(v-v')\frac{dp}{p} = 0 \quad (12)$$

If the volume of the liquid be neglected in comparison with that of the vapor, and the gas equation

$$pv = RT$$

be introduced, after division by T , the expression

$$\rho\frac{dT}{T^2} + AR\frac{dp}{p} = 0 \quad (13)$$

$$\text{or} \quad \rho\frac{dT}{T^2} + 2 \log p = 0 \quad (14)$$

is obtained. If this equation be integrated between the limits T and T_0 , it being admitted that the heat of vaporization is constant, the equation

$$2 \int_{T_0}^T \frac{dp}{p} + \int_{T_0}^T \rho \frac{dT}{T^2} = 0 \quad (15)$$

results, and, all calculations being made on the assumption that ρ is independent of T ,

* Bulletin de l'Académie royale de Belgique, III, ix, p. 281, 1885.

† The results of Ramsay's and Young's experiments show that $T\frac{dp}{dT}$ is constant for considerable differences of pressure. If it be true that $T\frac{dp}{dT}$ is constant then $\frac{\rho}{dv}$ must be constant also, for

$$\frac{dp}{dT} \cdot \frac{T}{A} = \frac{\rho}{dv}.$$

Ramsay and Young have also experimentally proven the truth of this relation. See Phil. Mag., V, xx, p. 515, 1885; *ibid.*, xxi, pp. 33 and 135; and *ibid.*, xxii, p. 33, 1886.

‡ Recherches expérimentales et théoriques sur les équilibres chimiques, Ann. des Mines, Mars-Avril, 1888, p. 337.

$$2 \log \frac{p}{p_0} + \rho \left(\frac{1}{T} - \frac{1}{T_0} \right) = 0. \quad (16)$$

This equation contains no constant, but if the terms T_0 and p_0 , which together form a constant, be transferred to the second member, the equation

$$2 \log p + \frac{\rho}{T} = \text{constant} \quad (17)$$

is obtained, and if the pressure be kept constant,

$$\frac{\rho}{T} = \text{constant}, \quad (18)$$

or, if ρ be taken as the heat of vaporization of the unit of mass of liquid,

$$\frac{\mu \rho}{T} = \text{constant}. \quad (18 \text{ bis})$$

It is seen from the foregoing that the constancy of the quotient of the molecular heat of vaporization by the absolute temperature at which the vaporization takes place has been arrived at by various scientists in different ways. This in itself is strong warrant for the truth of the relation. Still there exist certain discrepancies between the theory and the experimental determinations, which must be accounted for. Before taking up their consideration, however, it is necessary to pass in review what experimental work has been done.

II.

In Table I are given the latent heats of vaporization of a number of liquids, which have been determined by direct experiment at or near the ordinary atmospheric pressure. Only such liquids as are chemical units are admitted, solutions of acids and the like being excluded; also the determinations made with very volatile liquids, such as ammonia, sulphur dioxide, etc., are omitted. With these exceptions it is believed that no omissions of importance have been made.

The first column refers to the "References;" the second column (*a*) gives the name of the liquids; the third (*b*) their formula, and the fourth (*c*) their molecular masses; in the fifth (*d*) and sixth (*e*) columns are contained the temperatures at which vaporization took place and the latent heats for one gram of the liquid in heat units of which one warms one gram of water from 0° to 1° C., while the seventh (*f*) column shows the quotient obtained by dividing the molecular heat of vaporization by the absolute temperature. The eighth column (*g*) gives the pressure in rounded millimeters of mercury; when the pressure has not been indicated by the investigator, the space has been left vacant; however, from the nature of the methods, the pressure cannot vary greatly from normal atmospheric pressure.

TABLE I.

	Name.	Formula.	Molec- ular Mass.	Temp.	Latent Heat.	$\frac{\mu\rho}{T_{abs}}$	Pres- sure.
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>
I	Bromine	Br ₂	160	58	45·6	22·04	752
XIV	"	"	160	61·6	43·7	20·95	---
XX	Sulphur	S ₈	32 ₈	316	362·0	19·66	760
XX	Mercury	Hg	200	350	62·0	19·90	760
I	Phosphorus chloride ..	PCl ₃	137·3	78·5	51·4	20·07	750
I	Tin tetrachloride	SnCl ₄	259·5	112·5	30·5	20·49	753
XVIII	*Sulphur chloride	S ₂ Cl ₂	135	136	49·4	16·30	---
I	Carbon bisulphide	CS ₂	76	46·2	86·7	20·64	758
XXVIII	"	"	76	46·1	83·8	19·96	---
XXIV	"	"	76	46·6	85·7	20·37	759
XXVIIa	Diethylamine	C ₄ H ₁₁ N	73	58	61·0	20·07	---
IV	*Amylene	C ₈ H ₁₀	70	12·5	75·0	18·49	---
XXVI	Benzene	C ₆ H ₆	78	80·35	93·4	20·63	765
XXVIII	"	"	78	80·1	92·9	20·50	---
XXVI	Toluene	C ₇ H ₈	82	110·8	83·6	20·02	765
XXVI	Ethylbenzene	C ₈ H ₁₀	106	134·7	76·4	19·86	757
XXVI	Propyl benzene	C ₉ H ₁₂	120	157·0	71·8	20·00	754
XXVI	Metaxylene	C ₈ H ₁₀	106	139·9	78·3	20·09	766
XXVI	Pseudocumol	C ₉ H ₁₂	120	168·0	72·8	19·58	764
XXVI	Cymol	C ₁₀ H ₈	134	175·0	66·3	19·83	755
XI	Methylene chloride	CH ₂ Cl ₂	84·7	41·6	75·3	20·25	---
XXVIII	Chloroform	CHCl ₃	119·1	60·9	58·5	20·84	---
XXVIII	Carbon tetrachloride ..	CCl ₄	153·6	76·4	46·4	20·35	---
XXIII	"	"	153·6	76·4	46·6	20·49	758
I	Methyl iodide	CH ₃ I	141·5	42·2	46·2	20·66	751
XI	Ethylidene chloride	C ₂ H ₄ Cl ₂	98·7	60	67·0	19·88	---
XXIV	Ethyl chloride	C ₂ H ₅ Cl	64·4	21·17	89·3	19·59	---
XXVIII	" bromide	C ₂ H ₅ Br	109	38·2	60·4	21·15	---
VIII	"	"	109	38·4	61·6	22·25	---
I	" iodide	C ₂ H ₅ I	155·5	71·3	46·9	21·16	742
VIII	Ethylene bromide	C ₂ H ₄ Br ₂	188	131	43·8	20·38	---
VIII	*Amyl chloride	C ₅ H ₁₁ Cl	106·5	107	56·3	15·78	---
VIII	*Amyl bromide	C ₅ H ₁₁ Br	151	129	48·3	18·14	---
VIII	*Amyl iodide	C ₅ H ₁₁ I	197·5	156	47·5	21·87	---
I	*Methyl formiate	C ₂ H ₄ O ₂	60	32·9	117·1	22·96	752
X	* "	"	60	33(?)	115·2	22·58	---
I	*Ethyl "	C ₃ H ₆ O ₂	74	54·3	105·3	26·86	752
X	* "	"	74	53·5(?)	100·4	22·75	---
XXVI	"	"	74	53·5	92·2	20·88	753
XXVI	Propyl "	C ₄ H ₈ O ₂	88	81·2	85·3	21·18	760
XXVI	Isobutyl "	C ₅ H ₁₀ O ₂	102	98·0	77·0	21·17	759
XXVI	Isoamyl "	C ₆ H ₁₂ O ₂	116	124·0	71·7	20·93	759
XXVI	Methyl acetate	C ₃ H ₆ O ₂	74	57·3	94·0	21·04	757
I	* "	"	74	55·0	110·2	24·86	---
I	*Ethyl "	C ₄ H ₈ O ₂	88	74·6	92·7	23·46	---
XXVI	"	"	88	77·0	83·1	20·88	760
XXVIII	"	"	88	73·1	84·3	21·43	---
XXVI	Propyl "	C ₅ H ₁₀ O ₂	102	102·3	77·3	21·00	760
XXVI	Isobutyl "	C ₆ H ₁₂ O ₂	116	116·8	69·9	20·83	761
XXVI	Isoamyl "	C ₇ H ₁₄ O ₂	130	142·0	66·4	20·78	757
XXVI	Methyl propionate	C ₄ H ₈ O ₂	88	80·0	84·2	20·97	760
XXVI	Ethyl "	C ₅ H ₁₀ O ₂	102	98·7	77·1	21·15	759

TABLE I—*Continued.*

	Name.	Formula.	Molec- ular Mass.	Temp.	Latent Heat.	$\frac{\mu\rho}{T_{abs}}$	Pres- sure.
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>g</i>
XXVI	Propyl propionate	$C_8H_{16}O_2$	116	122.6	71.5	20.96	759
XXVI	Isobutyl "	$C_7H_{14}O_2$	130	136.8	66.0	20.96	760
XXVI	Isoamyl "	$C_8H_{16}O_2$	144	160.5	63.1	20.94	755
XXVI	Methyl butyrate	$C_8H_{16}O_2$	102	102.3	77.3	20.70	760
XXVI	Ethyl "	$C_8H_{16}O_2$	116	119	71.5	21.15	751
XXVI	Propyl "	$C_7H_{14}O_2$	130	143.6	66.2	20.65	761
XXVI	Isobutyl "	$C_8H_{16}O_2$	144	156.7	61.9	20.74	756
XXVI	Isoamyl "	$C_9H_{18}O_2$	158	178.0	59.4	20.80	761
XXVI	Methyl isobutyrate	$C_8H_{16}O_2$	102	92.5	75.5	21.06	757
XXVI	Ethyl "	$C_8H_{16}O_2$	116	110.0	69.2	20.96	758
XXVI	Propyl "	$C_7H_{14}O_2$	130	134.0	63.9	20.36	759
XXVI	Isobutyl "	$C_8H_{16}O_2$	144	148.6	59.9	20.47	760
XXVI	Isoamyl "	$C_9H_{18}O_2$	158	168.0	57.7	20.65	758
XXVI	Methyl valerate	$C_8H_{16}O_2$	116	116.3	69.9	20.83	758
XXVI	Ethyl "	$C_7H_{14}O_2$	130	134.0	64.7	20.67	758
XXVI	Propyl "	$C_8H_{16}O_2$	144	155.5	61.2	20.56	758
XXVI	Isobutyl "	$C_9H_{18}O_2$	158	169.0	57.9	20.69	760
XXVI	Isoamyl "	$C_{10}H_{20}O_2$	172	187.5	56.2	20.99	763
I	*Ethyl oxalate	$C_6H_{10}O_4$	146	184.4	72.7	23.22	756
XI	Ethylene oxide	C_2H_4O	44	13.5	138.6	21.28	----
XV	Ethyl oxide	$C_4H_{10}O$	74	34.9	89.9	21.63	----
I	" "	"	74	34.9	90.5	21.75	----
XXVIII	" "	"	74	34.5	88.4	21.27	----
XXII	" "	"	74	34.8	84.5	20.31	----
	Methylal	$C_3H_8O_2$	76	42.0	89.9	21.54	----
XVII	Water	$(H_2O)_x$	18 _x	99.8	535.8	25.87	----
I	"	"	18 _x	100	535.9	25.85	760
XXV	"	"	18 _x	100	532.0	25.67	----
XXVIII	Methyl alcohol	$(CH_4O)_x$	32 _x	64.5	267.5	25.36	----
XVII	"	"	32 _x	66.5	263.9	24.87	----
XVII	Ethyl "	$(C_2H_6O)_x$	46 _x	78.4	208.9	27.34	----
I	"	"	46 _x	77.9	202.4	26.53	759
XXV	"	"	46 _x	78.0	206.4	27.04	----
XXVIII	"	"	46 _x	78.1	205.0	26.85	----
XIXa	"	"	46 _x	78.3	201.4	26.37	----
XIXa	Propyl "	$(C_3H_8O)_x$	60 _x	96.9	164.1	26.61	----
XIXa	Isopropyl "	$(C_3H_8O)_x$	60 _x	82.2	159.7	26.98	----
XIXa	Butyl "	$(C_4H_{10}O)_x$	74 _x	116.5	138.2	26.25	----
XIXa	Isobutyl "	$(C_4H_{10}O)_x$	74 _x	107.7	136.2	26.47	----
XVII	Amyl "	$(C_5H_{12}O)_x$	88 _x	131(?)	121.4	26.44	----
XXV	"	"	88 _x	131	120.0	26.13	----
XIXa	"	"	88 _x	130.1	118.2	25.79	----
	Dimethylethyl carbinal	$(C_6H_{12}O)_x$	88 _x	102.1	110.4	25.90	----
XVII	Cetyl alcohol	$(C_{16}H_{34}O)_x$	242 _x	360(?)	58.5	22.36	----
XXVIII	Acetone	$(C_3H_6O)_x$	58 _x	56.6	125.3	22.05	----
XVII	Formic acid	$(CH_2O_2)_x$	46 _x	100	120.7	14.88	----
X	"	"	46 _x	100	103.7	12.78	----
XII	Acetic "	$(C_2H_4O_2)_x$	60 _x	118	84.9	13.03	----
XVII	Butyric "	$(C_4H_8O_2)_x$	88 _x	164	114.7	23.09	----
XVII	Valeric "	$(C_5H_{10}O_2)_x$	102 _x	175	103.5	23.57	----
XIa	Nitromethane	$C_1H_3NO_2$	60	101	116.7	18.71	----
XIa	Nitroethane	$C_2H_5NO_2$	75	113	92.0	17.72	----

REFERENCES.

- I, Andrews, Th., *Quart. Journ. Chem. Soc.*, London, i, 27, 1849.
 II-XI, Berthelot. *Comptes Rendus*. lxxviii, 162, 1874; *Annales de Chimie et de Physique*. v, vi, 145, 1875. III, *Comptes Rendus*, lxxxii, 119, 1876. IV, *ibid.*, p. 122. V, *Annales de Chimie et de Physique*, v, xii, 529, 1877. VI, *ibid.*, p. 535. VII, *ibid.*, p. 550. VIII, *Comptes Rendus*, lxxxviii, 52, 1879. IX, *ibid.*, lxxxix, 119, 1879. X, *ibid.*, xc, 1510, 1880. XI, *ibid.*, xciii, 118, 1881.
 XIa, Berthelot and Matignon, *Bull. Soc. Chim.*, III, xi, p. 867, 1894.
 X-XIV, Berthelot and J. Ogier, *Ann. Chim. Phys.*, V, xxiii, 201, 1881. XI, *Comptes Rendus*, xcii, 769, 1881. XII, *Ann. Chim. Phys.*, V, xxx, 382, 1883. XIII, *ibid.*, p. 400. XIV, *ibid.*, p. 410.
 XV, Brix, W., *Poggendorff's Annalen*, lv, 341, 1842.
 XVI, Dieterici, C., *Wiedemann's Annalen*, xxxvii, 494, 1889.
 XVII, Favre and Silbermann, *Ann. Chim. Phys.*, III, xxxvii, 461, 1853.
 XVIIa, Nadejdine, *Exner, Repertorium*, p. 446, 1894.
 XVIII, Ogier, *Comptes Rendus*, xx, 922, 1881. XIX, *ibid.*, xcvi, 646, 1883.
 XIXa, Longuinine, *Comptes Rendus*, cxix, 601, 1894.
 XX, Person, *Comptes Rendus*, xxiii, 343, 1846.
 XXI, Petit, *Ann. Chim. Phys.*, VI, xviii, 145, 1889.
 XXII, Ramsay and Young, *Philosophical Transactions*, clxxviii, A, 313, 1887.
 XXIII, Regnault, *Mémoires de l'Académie*, xxvi, 761, 1862. XXIV, *Id.*, *Ann. chim. phys.*, IV, xxiv, 375, 1871.
 XXV, Schall, *Ber. deutsch. chem. Ges.*, xvii, 2199, 1884.
 XXVI, Schiff, R., *Liebig's Annalen*, cxxxiv, 338, 1886.
 XXVII, Winkelmann, A., *Wiedemann's Annalen*. ix, 208 and 358, 1880.
 XXVIII, Wirtz, K., *Wiedemann's Annalen*, xl, 438, 1890.

It is not easy to make an estimate of the accuracy of some of the data recorded in the foregoing table; the determinations have been made by scientists employing different methods and different preparations, and hence the same degree of exactitude cannot be attributed to the work of each. Two principal sources of error are encountered in the determinations of latent heats of vaporization: the method may not be accurate: the liquid may not be pure. As a rule, in the same investigation both these sources of error are met with; that is, those investigators who have worked by faulty methods have also not always taken liquids of requisite purity. Nearly all the earlier determinations are subject to this criticism, as those by Person, Brix, and, to some extent, especially as regards the purity of the products, those by Favre and Silbermann. Andrews' work which, as far as the method is concerned, is remarkably accurate for the time when it was done, has been performed in some cases with impure liquids; this is especially true of the ethers investigated by him. Schiff states how difficult it is to obtain in a state of great purity the more volatile ethers. Thus, for ethyl formiate, a liquid very hard to purify, Schiff found the heat of vaporization to be 92.15 cal., while Andrews found 105.3 cal. With the exception of the ethers, however, Andrews' determinations may be regarded as very precious data. Of the purity of the liquids used by Berthelot and by Ogier, it is especially hard to form an opinion, inasmuch as these scientists have not indicated with but few exceptions

their methods of purification. If it be permitted to judge from a single example taken at random, we cannot admit that their products were always as pure as necessary; thus, they found for the latent heat of vaporization of ethyl formate, which, as stated just above, Schiff determined to be 92.15 cal., equal to 100.4 cal. The impurity within compounds of the ether class is for the most part water. Since water requires much more heat for vaporization than most liquids, its presence, even in minimal amount, exercises considerable influence upon the value of a determination. In those cases, therefore, where water may be present as impurity, the heat of vaporization will be too high. And, as a matter of fact, the determinations on the ethers made by Andrews, as well as by Berthelot and by Ogier, all give values higher than those found by Schiff, who took the greatest pains to fully rid his preparations of water. The method employed by them is, however, quite beyond any but the sharpest criticism, so that their determinations may be admitted as sufficiently accurate with the exception of the amyl halogen compounds, anylene, ethyl formate, and sulphur chloride. The work of the other investigators may be admitted without question, especially that due to Schiff, which is a marvel of accuracy. Such determinations as are not trustworthy are marked in the table with a star.

III.

An inspection of Table I shows that the numbers in column *f* are quite constant, with the exception of the alcohols, the acids, and the nitro-compounds, as well as water and acetone. Leaving these liquids aside for a moment,—their seemingly irregular behavior will be explained away later on—we will consider the various family of compounds of which Table I is made up. Taking all the reliable determinations into consideration, we find that the average value of the “constant” is for about seventy liquids equal to 20.70, the greatest value being 22.04 for bromine (Andrews I).^{*} For the elements and inorganic compounds, the “constant” is equal to 20.41 with 22.04 and 19.66 as extreme values; for the hydrocarbons, to 20.19, 20.63 and 19.58 being the extreme values; for the halogen compounds, to 20.63, with extreme values equal to 21.16 and 19.59; for the esters, to 20.87, the extremes being 21.43 and 20.36. With the exception of the esters, the determinations have been made by different men in different ways, so that a great degree of “constancy” is hardly to be expected; yet the

^{*} The determination by Berthelot and Ogier (xiv), however, gives 20.95 as the value of the “constant,” so that it is perhaps better to reject Andrews' determination. If that be done the greatest value is 21.54 for methylal (Berthelot) and the smallest value being 19.58 for pseudocumene (Schiff).

"constant" is remarkably constant. Schiff's work was most carefully done by the same method and hence his results are at once reliable and comparable in an eminent degree; and, as a matter of fact, the extreme values of the constant calculated from his data differ from the average value by hardly three per cent.

Such a regularity as the above implies that the liquids at their boiling points are in corresponding states (the term "corresponding states" being used in the sense given it by van der Waals (*loc. cit.*) As far as the pressure is concerned, it may be stated that atmospheric pressure can be reckoned as "corresponding" in questions of this sort. That boiling points for certain properties of liquids are "corresponding temperatures" in a not inconsiderable measure has been shown by C. M. Guldberg* who in comparing the quotient of the absolute boiling points by the absolute critical temperature found it to remain close to an average value of about $\frac{2}{3}$, and concluded that quantities which vary slowly with the temperature (among which latent heats of vaporization are to be counted) may be reckoned as being approximately in corresponding states at their points of ebullition. This conclusion follows directly from equation (4) which indicates that the relation

$$\frac{\rho\mu}{T_1} = \psi \frac{T}{T_1} \quad (19)$$

must obtain (ψ being an unknown function). Guldberg then states that through comparison of various liquids the equation

$$\psi\left(\frac{2}{3}\right) = 14 \quad (20)$$

is found by means of graphic interpolation, and accordingly at the boiling points the relation

$$\frac{\rho\mu}{T_1} = 14 \quad (21)$$

obtains with a certain approximation. Inasmuch as

$$\frac{T}{T_1} = \frac{2}{3},$$

it follows that

$$\frac{\rho\mu}{T} = 21. \quad (22)$$

Guldberg thus obtains about the same "constant" as has been shown in the foregoing to be the average of reliable determinations.

As stated above, the values of $\frac{\mu\rho}{T}$ given in the table differ

* Zeitschr. für phys. Chemie, v, p. 374, 1890.

considerably from the normal average value in the case of the acids, nitro-methane and nitro-ethane, the alcohols, acetone and water. For the acids and nitro-compounds they are too small; for the alcohols, water, and acetone, they are too large. The cause of this abnormal behavior is to be found in the "association" of the molecules of these liquids, and in the changes which the molecular aggregations undergo during the process of vaporization. We will consider the case of the alcohols, water, and acetone first.

The brilliant experiments of Ramsay and his associates on the surface tensions of liquids, and his theoretical deductions have taught us that the liquids in question are made up of molecules in a state of association. No facts are known, however, which indicate that an appreciable amount of molecular association is persistent in the vaporous state; on the contrary, the normality of the vapor density, and other properties of the vapors, show that they consist exclusively, it may be said, of simple molecules. Accordingly, when the alcohols, etc., are evaporated, there occurs a decomposition of the complex molecules into simple ones. This requires the expenditure of a certain amount of energy, which is manifest as heat energy. The heat necessary to convert a molecularly polymerized liquid into its normal vapor consist then of two terms,* the heat expended in actually turning the liquid into a gas, and the heat used up in decomposing the molecular aggregations or "tag-mas." The value of ρ , then, in the expression $\frac{\rho\mu}{T} = \text{const.}$ is

greater for associated than for normal liquids; hence the value of the "constant" becomes greater, and, indeed, so much the greater, the more complex the liquid molecule. It seems at present impossible to make a reliable correction for the heat employed in decomposing the complex molecules.

In the case of the acids, the state of affairs is somewhat different. It has long been known that the organic acids, as formic, and acetic acid, have abnormal vapor densities due to the association of the molecules in the vaporous state; as the temperature rises, the degree of association becomes less and less until the normal molecule is reached. At the boiling points under ordinary atmospheric pressure, the vapor density of formic acid may by extrapolation from the data due to Petersen and Ekstrand† be put at 2.5 at 100°; this multiplied by 28.87 gives a molecular mass of 72; and this value of μ when introduced into the relation $\frac{\mu\rho}{T_{\text{abs}}} = \text{const.}$, gives for the

* See Guye's paper: Sur la polymérisation moléculaire des liquides: *Archives des Sciences physiques et naturelles*, III, **xxxi**, 160, 1894.

† *Ber. der deutschen chem. Gesell.*, **xiii**, 1194.

"constant," 19.89. Likewise from extrapolation of Cahours* determinations of the vapor density of acetic acid, its vapor density at 118° may be set at 3.3, which by multiplication by 28.87 gives as molecular mass 95; and this in turn shows the value of the "constant" to be 20.34. Now we have every reason to believe that the gaseous associated molecule does not dissociate on passing into the liquid state; on the contrary, there can scarcely be any doubt but that it increases more or less in complexity. Accordingly, the molecular masses calculated for the gaseous molecules may be set as very near those of the liquid molecules of the two acids in question, and, indeed, the experiments of Schall† indicate that for acetic acid, at least, such is the state of affairs. The values of the "constant" found for these corrected molecular masses are seen to be practically identical with that found for normal liquids, and the exception presented by the acids is seen to be but seeming. For butyric and valeric acids, however, the "constants" cannot be corrected as for the two preceding acids, since they are found to be too large even when calculated on the assumption that their molecular masses are normal. If their determinations of latent heat of volatilization are sufficiently accurate—which is somewhat doubtful—it is probable that the complex liquid molecules in their case undergo decomposition on passing into the vaporous state, similar to the alcohols, etc. In the absence of experiments on their vapor densities it is not possible to judge what is the true state of the case.

Nitromethane and nitroethane also give values of the constant less than the normal. Ramsay and Shields‡ have measured the superficial tension of nitroethane, finding it such as to legitimize the assumption that the molecules of this liquid are in a state of association; by analogy it may be admitted that nitromethane is also an associated liquid, although no experimental data are at hand. If what has been said in explanation of the seeming abnormality in the behavior of the acids as regards the "constant" be in accordance with fact, it is necessary to suppose that the two nitro-compounds also pass from the liquid into the gaseous condition without the complex molecule suffering much dissociation.

The immediately preceding considerations indicate a method of getting an approximation of the degree of association of a liquid. If any liquid, whose latent heat of volatilization be known, gives a value for the "constant" close to 20.7, it is pretty certain that it is normal. If it gives a less value, it is associated in the liquid as well as in the gaseous state; if it

* Comp. Rend., xix, 771.

† Ber. der deutschen chem. Gesell., xvii, 2199, 1884.

‡ Zeitschr. für phys. Chem., xii, 433, 1893.

gives a greater value, it must be associated in the liquid state alone. The greater the variation from the normal value of the "constant," the greater the amount of the association.

Thus far, we have considered the application of the formula

$\frac{\mu\rho}{T_{abs}} = \text{const.}$ only to determinations made under the pressure

of about one atmosphere. But how will it be at other pressures and hence other temperatures? All of the deductions of the formula have been made on the assumption that the pressure was that of one atmosphere, with the exception of the one developed by Le Chatelier, which contains a term referring to pressure (Equation 17). This equation, however, was derived on the supposition that the latent heat of vaporization is independent of temperature and pressure; such an assumption, however, does not accord with the experimental results obtained by Regnault, Ramsay and Young, Jahn, and others. The heat of vaporization of a liquid decreases with rise of temperature and concomitant increase of pressure until at the critical point it becomes equal to zero. Yet for all temperatures and concurrent pressures below the critical, the relation (17) obtains, and the lower the temperature, the larger the "constant." The number of reliable data at hand for the comparison of the theory with experiment at other pressures than the atmospheric is relatively small. Most of them have been made at the freezing point of water under the pressure of the saturated vapor at that temperature. In Table II are given such data as are reliable, and only for normal liquids. In the first column is given a reference number to the investigator's names and places of publication,—directly below the table. Columns *a*, *b*, *c*, and *d* give the name, formula, molecular mass, and the latent heat of vaporization, respectively of the liquids in question. The sixth (*e*) column contains the value of the

expression $\frac{\mu\rho}{T_{abs}}$, and the seventh (*f*) the value of twice the natural logarithm of the pressure. (The pressure in the case of such liquids as have had their vapor tension determined is generally set as equal to that of the saturated vapor at 0°; for the others, the pressure has been put at 60^{mm} of mercury, as Jahn, in his experiments, reduced the pressure to this point before allowing evaporation to take place, and the others examined by him have not been investigated thoroughly as regards their vapor tensions. The pressure is reduced to absolute measure by multiplication by 13.6.) The last column gives the value of Le Chatelier's relation (17), obtained by adding the values found in columns *e* and *f* for each liquid.

TABLE II.

Ref. No.	Name.	Formula.	Molecular Mass.	Latent Heat.	$\frac{\mu\rho}{T_{abs}}$	$2 \log p.$	
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>	<i>f and e</i>
I	Benzene.....	C ₆ H ₆	78	107·6	30·75	9·8	40·55
II	".....	"	78	109·0	31·14	9·8	40·94
II	Chloroform.....	CHCl ₃	119·4	67·0	29·20	12·85	42·05
II	Carbon tetrachloride..	CCl ₄	156	52·0	29·25	12·21	41·46
II	Carbon disulphide	CS ₂	76	90·0	25·00	14·92	39·92
III	".....	"	76	89·5	25·09	14·92	40·07
III	Ethyl ether.....	(C ₂ H ₅) ₂ O	74	93·5	25·21	15·67	40·87
II	".....	"	74	94·0	25·49	15·67	41·16
I	Ethyl formiate.....	C ₃ H ₈ O ₂	74	113·25	30·69	9·8	40·49
I	Propyl formiate.....	C ₄ H ₈ O ₂	88	105·37	33·96	9·8	43·76
I	Methyl acetate.....	C ₃ H ₆ O ₂	74	113·86	30·86	9·8	40·09
I	Ethyl acetate.....	C ₄ H ₈ O ₂	88	102·14	32·92	9·8	42·72

I, Jahn, Zeitschr. f. phys. Chem., xi, 790, 1893.

II, Regnault, Memoires de l'Académie, xxvi, 761, 1862.

III, Winkelmann, Wiedemann's Annalen, ix, 208 and 358, 1880.

Table II shows that, while it is impossible to speak of a constancy for the values contained in the sixth column, through the introduction of the pressure correction in equation (17) a value is found equal in mean to about 40·5; it is remarkable that such a constancy is to be found in the values, since no great amount of accuracy can be attributed to the determinations of the latent heat or of the pressure. If the pressure correction be applied to the determinations of the latent heats of vaporization carried out under or nearly under atmospheric pressure, the "constant" is found to become equal to 39·18, since $2 \log 760$ equals 18·48; this value, as is to be expected, is very near to that found for the liquids under the circumstances given in table II; undoubtedly, approximately the same value for the expression would be found under other pressures and concurrent temperatures, although the data at hand are too meager to make it worth while to perform the necessary calculations. As a conclusion to all that precedes and as a prediction of all future experimental work on latent heats of vaporization, it may be stated that the relation deduced by Le Chatelier may be put equal to about 40·00, thus

$$2 \log p + \frac{\mu\rho}{T_{abs}} = 40\cdot00 \quad (17 \text{ bis})$$

IV.

In accurate determinations of temperatures of ebullition, it is often necessary to make a correction for the variation of the pressure from the normal pressure of 760^{mm} of mercury. In

case the latent heat of vaporization of the liquid under examination is known, this correction is easily made by the application of equation (1), which gives in terms of latent heat, temperature, and volume, the change of the boiling point with the concomitant variation of pressure. But the latent heats of volatilization are known for only a comparatively small number of liquids. In this case, the "law" treated of in the foregoing sections is specially applicable. We know from what precedes that near atmospheric pressure

$$\frac{\mu\rho}{T_{abs}} = \text{const.}, \quad (\text{A})$$

The "constant" varying slightly for different classes of liquids from an average value of 20.7, at least, for normal liquids. If we set for the "constant," the letter C, neglect the volume of the liquid in comparison with that of the vapor—which will introduce no appreciable error,—and substitute for T its equal $\frac{\mu\rho}{C}$, equation (1) becomes transformed into

$$\frac{dT}{dp} = \frac{v\mu}{C}. \quad (\text{B})$$

If now, from the gas equation

$$v = \frac{2T}{p} \quad (\text{C})$$

we take the value of $\mu\rho$ ($\mu\rho = V$ = a gram-molecule of saturated vapor), and set it in equation (B), we obtain the equality

$$\frac{dT}{dp} = \frac{2T}{pC}; \quad (\text{D})$$

and if p be the normal pressure of 760^{mm}, we get finally

$$\frac{dT}{dp} = \frac{2T}{760\text{ C}} = \frac{T}{380\text{ C}}, \quad (\text{E})$$

or

$$dT = \frac{T}{380\text{ C}} \cdot dp. \quad (\text{F})$$

By putting for C, that value of the constant found for the class of liquids to which the liquid under examination belongs (see page 359), and for T, the absolute temperature of ebullition, we may obtain with a very considerable degree of accuracy the desired correction, with the restriction, however, that the variation of pressure is but slight, that is, not over 50 millimeters of mercury.

Chicago, January 22d, 1895.