

pended matter at the time of the taking of the sample, but owing to the finely divided state and the dark color of the water it escaped notice unless the sample stood quietly for some time. The bottom of the pool was covered with this precipitate or milk of sulphur. It is therefore possible that it may have come from hydrogen sulphide, although there was no evidence of the presence of the gas when the sample was taken. Tests for the presence of arsenic and the rare elements gave negative results.

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VAPOR-PRESSURE AND CHEMICAL COMPOSITION.

BY EUGENE C. BINGHAM.

Received March 27, 1906.

ACCORDING to the theory of corresponding conditions, the calculation of the vapor-pressure curve is possible by means of some equation of the form

$$\frac{p}{\pi} = \int \left(\frac{T}{\tau} \right)$$

where π and τ represent the critical pressure and critical temperature respectively. $\int \left(\frac{T}{\tau} \right)$ is then a temperature function which is independent of the nature of the substance under consideration. Van der Waals¹ gave, as a first approximation to this function, the form

$$\log \frac{\pi}{p} = a \left(\frac{\tau}{T} - 1 \right) \dots (1)$$

where a has the same value for all substances. Van der Waals found this to be about 3.0. Considering the simplicity of the formula, the approximation is remarkable; yet the values of a are not the same for different substances and the values vary somewhat also with the temperature.

To investigate this point more fully Nernst² plotted curves for a number of substances, using values of $\log \frac{\pi}{p}$ as ordinates and of $\frac{\tau}{T} - 1$ as abscissae. It was found that the slope of the curves increases quite regularly with the molecular weight of the substances. It is at least apparent that the curves of all substances do not fall together into a single straight line as the theory of

¹ Kontinuität, p. 148.

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

corresponding condition demands. Moreover, the curves of substances of very small molecular weight, bend toward the X-axis as the values of $\frac{\tau}{T} - 1$ increase while those of the substances of large molecular weight bend in the opposite direction. Following the suggestion of Prof. Nernst I have plotted curves for a large number of substances and have found the same characteristics present.

Even if the function $\int \left(\frac{T}{\tau} \right)$ is not *the same* for all substances, it may be of the same *nature* for all, only having different numerical constants, from substance to substance. The vapor-pressure curve, in this case, would be determined when we knew the critical temperature and pressure and in addition a single point of the vapor-pressure curve as, for example, the boiling-point. Nernst¹ has given as an expression of this function the form

$$\ln \frac{\pi}{p} = m \ln \frac{\tau}{T} + \alpha' \left[\left(\frac{\tau}{T} - 1 \right) - \frac{1}{n} \left(1 - \frac{T}{\tau} \right) \right]$$

where m and n are constants for all substances and α' a constant varying with the nature of the substance. I have given considerable effort to finding the best values for these constants and to trying the effect of adding another term, but have found no form more satisfactory than that given by Nernst as cited above,

$$\log \frac{\pi}{p} = 1.75 \log \frac{\tau}{T} + \alpha' \left[\left(\frac{\tau}{T} - 1 \right) - \frac{1}{2.36} \left(1 - \frac{T}{\tau} \right) \right] \dots (2)$$

Since $\alpha' \left(\frac{\tau}{T} - 1 \right)$ is the most important term, the above equation is seen to be a development of Van der Waals' equation (1). Indeed, for medium values of α' the terms $1.75 \log \frac{\tau}{T}$ and $\frac{\alpha'}{2.36} \left(1 - \frac{T}{\tau} \right)$ nearly counteract each other. There are deviations in the region of the critical temperature, but we can only expect equation (2) to hold at low temperatures where the vapor obeys the gas laws.

In the following tables the values of α' and of $M\alpha'$ (where M is the molecular weight) are given for a large number of substances as calculated from the temperature of their boiling-points under atmospheric pressure and the critical date.

In order to show the regularities inherent in these values,

¹ Loc. cit.

“atomic” values for each element have been calculated, the substance used for this purpose being enclosed in brackets in Table I. The value for carbon is a mean value, approximately that of pentane. From the atomic values, the molecular values, Ma' , for the different compounds are calculated by addition and compared with the observed values. Thus, if any compound is represented by the formula



where l, m, n, \dots are the number of atoms of carbon, hydrogen, oxygen, \dots respectively in the molecule, then

$$Ma' = 42l + 1.9m + 4In + 34.40 + 85p + 46q + 98r + 236s + 38It + 85.4u + 195v + 297w + 306x + 201y + 460z \dots (3)$$

The agreement is perhaps as good as we ought to expect. The differences among the isomers are partly due to constitutive influences which have not been taken into account in the formula. In the series of aliphatic hydrocarbons, the observed values of Ma' increase more rapidly than those calculated by the formula. This is reminiscent of the effect of constitutive influences which is met with in considering the molecular volumes¹ of these substances. Further, it is certain that equation (2) is only a rough approximation so it is sufficient for the present to have shown that these quantitative constitutive influences are present.

TABLE I.²

Substance.	Formula.	. M.	π atm.	τ abs.	α' .	Ma' .	Ma' calc.	Diff.
Hydrogen	H ₂	2.0	14.2	32.2	1.92	3.8	[3.8]	
Argon.....	Ar	39.9	52.9	155.6	2.14	85.0	[85.]	
Methane.....	CH ₄	16.0	55.2	191.2	2.26	36.0	50	—14
Xenon.....	Xe	128.0	57.2	287.8	2.32	297	[297]	
Carbon monoxide ...	CO	28.0	35.5	137.4	
Krypton.....	Kr	81.8	54.3	210.5	2.38	195	[195]	
Nitrogen	N ₂	28.1	27.5	124.0	2.45	69	[69]	
Hydrogen selenide...	H ₂ Se	81.2	91.0	411.0	2.52	205	[205]	
Oxygen.....	O ₂	32.0	50.8	154.2	2.55	82	[82]	
Chlorine	Cl ₂	70.9	93.5	419.0	2.77	196	[196]	
Carbon disulphide...	CS ₂	76.1	77.8	548.0	2.79	212	[212]	
Carbon tetrachloride	CCl ₄	153.8	44.97	556.15	2.99	460	435	25
Ammonia	NH ₃	17.1	107.6	404.0	3.02	52	41	11
Benzene.....	C ₆ H ₆	78.0	47.89	561.5	3.07	239	263	—24
Hexamethylene	C ₆ H ₁₂	84.1	39.82	552.95	3.08	259	275	—16
Diisopropyl.....	C ₆ H ₁₄	86.1	30.72	500.4	3.19	275	279	— 4

¹ Van't Hoff: Theoretische Chemie, Vol. III, p. 32, 2d ed.

² Landolt and Börnstein's tables.

TABLE I—Continued.

Substance.	Formula.	M.	π atm.	τ abs.	α' .	$M\alpha'$.	$M\alpha'$ calc.	Diff.
Pentane.....	C_5H_{12}	72.1	33.03	470.2	3.21	231	233	— 2
Phenyl iodide.....	C_6H_5I	204.0	42.62	721.0	3.15	643	[643]	
Phenyl chloride.....	C_6H_5Cl	112.5	44.62	633.0	3.18	358	360	— 2
Phenyl fluoride.....	C_6H_5F	96.1	44.62	559.6	3.20	308	[308]	
Methyl formate.....	$C_2H_4O_2$	60.0	59.24	487.0	3.22	193	173	20
Stannic chloride.....	$SnCl_4$	260.8	36.95	591.7	3.27	853	[853]	
Ether.....	$C_4H_{10}O$	74.1	35.61	467.4	3.29	244	228	16
Hexane.....	C_6H_{14}	86.1	29.62	507.8	3.38	291	279	12
Acetone.....	C_3H_6O	58.0	60.0	510.5	3.53	205	223	—18
Water.....	H_2O	18.0	194.6	638.0	3.80	68	45	23
Ethyl acetate.....	$C_4H_8O_2$	88.1	37.94	523.1	3.61	318	265	53
Acetic acid.....	$C_2H_4O_2$	60.0	57.11	594.6	3.85	231	173	58
Methyl butyrate.....	$C_5H_{10}O_2$	102.1	34.21	554.25	3.66	374	311	63
Octane.....	C_8H_{18}	114.1	24.70	569.2	3.69	421	370	51
Methyl alcohol.....	CH_3O	32.0	78.63	513.0	4.22	135	90	45
Ethyl alcohol.....	C_2H_5O	46.0	62.76	516.6	4.50	207	136	71
Propyl alcohol.....	C_3H_7O	60.1	50.16	536.7	4.45	267	182	85
Isobutyl alcohol.....	$C_4H_{10}O$	74.1	48.27	538.0	4.87	361	228	133

TABLE II.

Substance.	Formula.	M.	π atm.	τ abs.	α' .	$M\alpha'$.	$M\alpha'$ calc.	Diff.
Methane.....	CH_4	16.0	55.2	191.2	2.26	36	50	—14
Ethane.....	C_2H_6	30.0	45.2	308.0	2.47	74	95	—21
Ethylene.....	C_2H_4	28.0	53.5	282.8	2.76	77	92	—15
Propane.....	C_3H_8	44.1	44.	370	3.14	138	141	— 3
Pentane.....	C_5H_{12}	72.1	33.03	470.2	3.21	231	233	— 2
Isopentane.....	C_5H_{12}	72.1	32.92	460.8	3.22	232	233	— 1
Isomylene.....	C_5H_{10}	70.1	33.9	464.6	3.34	234	229	5
Benzene.....	C_6H_6	78.0	47.89	561.5	3.07	239	263	—24
Hexamethylene.....	C_6H_{12}	84.1	39.82	552.95	3.08	259	275	—16
Hexane.....	C_6H_{14}	86.1	29.62	507.8	3.38	291	279	12
Diisopropyl.....	C_6H_{14}	86.1	30.72	500.4	3.19	275	279	— 4
Toluene.....	C_7H_8	92.1	41.6	593.6	3.22	297	309	—12
Heptane.....	C_7H_{16}	100.1	26.86	539.9	3.66	366	324	42
Xylene.....	C_8H_{10}	106.1	36.9	631.3	3.30	350	355	— 5
Xylene.....	C_8H_{10}	106.1	35.8	618.6	3.46	367	355	12
Xylene.....	C_8H_{10}	106.1	35.0	617.4	3.40	361	355	6
Ethylbenzene.....	C_8H_{10}	106.1	38.1	619.4	3.36	356	355	1
Diisobutyl.....	C_8H_{18}	114.1	24.55	549.8	3.58	408	370	38
Octane.....	C_8H_{18}	114.1	24.70	569.2	3.69	421	370	51
Mesitylene.....	C_9H_{12}	120.1	33.2	640.7	3.75	450	401	49
Propylbenzene.....	C_9H_{12}	120.1	32.3	638.6	3.50	420	401	19
Isopropylbenzene.....	C_9H_{12}	120.1	32.2	635.7	3.41	410	401	9
Pseudocumol.....	C_9H_{12}	120.1	33.2	654.2	3.60	432	401	31
Naphthalene.....	$C_{10}H_8$	128.1	39.2	741.2	3.50	448	435	13
Durene.....	$C_{10}H_{14}$	134.1	28.6	675.5	3.58	480	447	33
Isobutylbenzene.....	$C_{10}H_{14}$	134.1	31.1	650.1	3.54	475	447	28

TABLE II—Continued.

Substance.	Formula.	M.	π atm.	τ abs.	α' .	$M\alpha'$.	$M\alpha'$ calc.	Diff.
Decane.....	$C_{10}H_{22}$	142.2	21.3	603.4	4.55	647	462	185
Diphenyl.....	$C_{12}H_{10}$	154.1	31.8	768.6	3.74	576	523	53
Diphenylmethane....	$C_{13}H_{12}$	168.1	28.2	770.0	3.94	662	567	95

TABLE III.

Substance.	Formula.	M.	π atm.	τ abs.	α' .	$M\alpha'$.	$M\alpha'$ calc.	Diff.
Methylamine.....	CH_5N	31.1	72.0	428.0	3.37	105	86	19
Dimethylamine.....	C_2H_7N	45.1	56.0	436.0	3.49	157	132	25
Trimethylamine.....	C_3H_9N	59.1	41.0	433.5	3.07	181	178	3
Ethylamine.....	C_2H_7N	45.1	66.0	450.0	3.79	171	132	39
Diethylamine.....	$C_4H_{11}N$	73.1	39.3	491.0	2.63	192	223	-31
Triethylamine.....	$C_6H_{15}N$	101.2	30.0	532.0	3.51	355	315	40
Propylamine.....	C_3H_9N	59.1	50.0	491.0	3.67	217	178	39
Dipropylamine.....	$C_6H_{15}N$	101.1	31.0	550.0	3.94	398	315	83
Aniline.....	C_6H_7N	93.1	52.35	698.7	3.65	340	300	40
Dimethylaniline.....	$C_8H_{11}N$	121.1	35.8	687.45	3.71	449	391	58
Dimethylorthotolu- dine.....	$C_9H_{13}N$	135.1	30.8	667.8	3.65	493	437	56
Propionitrile.....	C_3H_5N	55.1	41.3	558.7	3.55	196	170	26
Butyronitrile.....	C_4H_7N	69.1	37.4	582.1	3.67	254	216	38
Capronitrile.....	$C_6H_{11}N$	97.1	32.15	621.8	3.77	366	307	59
Benzonitrile.....	C_7H_5N	103.1	41.6	699.0	3.59	370	338	32
Nitrous oxide.....	N_2O	44.1	74.0	308.9	2.86	126	110	16
Nitric oxide.....	NO	30.0	71.2	179.5	4.36	131	75	56

TABLE IV.

Substance.	Formula.	M.	π atm.	τ abs.	α' .	$M\alpha'$.	$M\alpha'$ calc.	Diff.
Methyl chloride.....	CH_3Cl	50.5	73.0	414.5	2.99	151	146	5
Chloroform.....	$CHCl_3$	119.4	54.9	533.0	3.17	379	338	41
Carbon tetrachloride	CCl_4	153.8	44.97	556.15	2.99	460	435	25
Ethylene chloride....	$C_2H_4Cl_2$	98.9	53.0	561.4	3.28	324	288	36
Ethylidene chloride.	$C_2H_4Cl_2$	98.9	52.4	528.0	3.19	316	288	28
Propyl chloride.....	C_3H_7Cl	78.5	49.0	494.0	3.43	269	238	31
Phenyl chloride.....	C_6H_5Cl	112.5	44.62	633.0	3.18	358	360	-2
Germanium tetra- chloride.....	$GeCl_4$	214.3	38.0	549.9	3.26	699	[699]	
Ethylene bromide....	$C_2H_4Br_2$	188.0	70.6	582.8	5.05	950	735	215
Thiophene.....	C_4H_4S	84.1	47.7	590.3	2.67	225	261	-36

TABLE V.

Substance.	Formula.	M.	π atm.	τ abs.	α' .	$M\alpha'$.	$M\alpha'$ calc.	Diff.
Methyl formate.....	$C_2H_4O_2$	60.0	59.35	487.0	3.22	193	173	20
Ethyl formate.....	$C_3H_6O_2$	74.1	46.83	508.3	3.30	244	219	25
Propyl formate.....	$C_4H_8O_2$	88.1	40.05	537.85	3.43	302	265	37
Amyl formate.....	$C_6H_{12}O_2$	116.1	34.12	575.6	4.20	488	356	132
Methyl acetate.....	$C_3H_6O_2$	74.1	46.29	506.7	3.47	257	219	38
Ethyl acetate.....	$C_4H_8O_2$	88.1	37.94	523.1	3.61	318	265	53
Propyl acetate.....	$C_5H_{10}O_2$	102.1	33.17	549.2	3.74	382	311	71

TABLE V—Continued.

Substance.	Formula.	M.	π atm.	τ abs	α' .	Ma' .	Ma' calc.	Diff.
Isobutyl acetate	$C_6H_{12}O_2$	116.1	31.4	561.3	3.92	455	356	99
Methyl propionate...	$C_4H_8O_2$	88.1	39.51	530.4	3.56	314	265	49
Ethyl propionate.....	$C_5H_{10}O_2$	102.1	33.17	545.9	3.71	379	311	68
Methyl butyrate.....	$C_5H_{10}O_2$	102.1	34.21	554.25	3.66	374	311	63
Ethyl butyrate.....	$C_6H_{12}O_2$	116.1	30.24	565.8	3.88	451	356	94
Methyl isobutyrate..	$C_5H_{10}O_2$	102.1	33.88	540.55	3.61	369	311	58
Ethyl isobutyrate....	$C_6H_{12}O_2$	116.1	30.13	553.4	3.82	444	356	88
Methyl valerate.....	$C_6H_{12}O_2$	116.1	31.5	566.7	4.23	491	356	135

TABLE VI.

Substance.	Formula.	M.	π atm.	τ abs.	α' .	Ma' .	Ma' calc.	Diff.
Methyl ether.....	C_2H_6O	46.1	57.0	402.6	3.07	142	136	6
Methyl ethyl ether...	C_3H_8O	60.1	46.27	441.4	3.28	197	182	15
Ether	$C_4H_{10}O$	74.1	35.61	467.4	3.29	244	228	16
Acetone	C_3H_6O	58.0	60.0	510.5	3.53	205	223	-18
Methyl alcohol.....	CH_4O	32.0	78.63	530.5	4.22	135	90	45
Ethyl alcohol.....	C_2H_6O	46.0	62.76	516.6	4.50	207	136	71
Propyl alcohol.....	C_3H_8O	60.1	50.16	536.7	4.45	267	182	85
Isopropyl alcohol....	C_3H_8O	60.1	53.1	507.6	4.91	295	182	13
Isobutyl alcohol.....	$C_4H_{10}O$	74.1	48.27	538.0	4.87	361	228	133
Cresol.....	C_7H_8O	108.1	45.0	705.0	3.94	426	350	76
Anisol	C_7H_8O	108.1	41.25	641.5	3.62	395	350	45
Water.....	H_2O	18.0	194.6	638.0	3.80	68	45	23
Acetic acid.....	$C_2H_4O_2$	60.0	57.11	594.6	3.85	231	173	58
Carbon dioxide.....	CO_2	44.0	72.9	304.35	3.15	139	124	15
Sulphur dioxide.....	SO_2	64.1	78.9	428.4	3.27	210	167	53

In Table I the substances are grouped according to the values of α' . It is seen that the elements of small molecular weight as hydrogen have the smallest values of α' and that they increase regularly up to the alcohols of high molecular weight and considerable association. Table II contains a large number of hydrocarbons grouped according to their complexity. Table III contains nitrogen compounds—amines, nitriles, and oxides of nitrogen. Table IV contains various halogen and sulphur compounds, while in Table V are grouped the esters, and in Table VI alcohols, acids and other oxygen compounds. In the associated compounds there is wide divergence between the observed and calculated values of Ma' .

CONCLUSION.

From the study of a large number of substances, Nernst's¹ equation

¹ Loc. cit.

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

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.

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.