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.

UNIVERSITY OF MINNESOTA, MINNEAPOLIS.

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

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

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

$$\log \frac{\pi}{p} = a \left(\frac{\tau}{T} - I\right) \quad . \quad . \quad (I)$$

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 $\frac{\tau}{T}$ — I 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

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

¹ Kontinuität, p. 148.

corresponding condition demands. Moreover, the curves of substances of very small molecular weight, bend toward the X-axis as the values of $\frac{\tau}{T} - I$ 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 $\alpha'\left(\frac{\tau}{T}-I\right)$ is the most important term, the above equation is seen to be a development of Van der Waals' equation (I). Indeed, for medium values of α' the terms 1.75 log $\frac{\tau}{T}$ and $\frac{\alpha'}{2.36}\left(I-\frac{T}{\tau}\right)$ 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, $M\alpha'$, for the different compounds are calculated by addition and compared with the observed values. Thus, if any compound is represented by the formula

$$C_1H_mO_nN_oS_pF_qCl_rBr_sI_tAr_uKr_vXe_wGe_rSe_vSn_z$$

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

 $M\alpha' = 42l + 1.9m + 41n + 34.40 + 85p + 46q + 98r + 236s +$

381t+85.4u+195v+297w+306x+201y+460z...(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 $M\alpha'$ 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.

| | | TA | BLE I. ² | | | | | |
|--------------------|--------------------------------|---------------|---------------------|----------------|-------|-------|-------------|---------|
| Substance. | Formula. | .м. | π atm. | au abs. | α'. | мα'. | Mα' cale | . Diff. |
| Hydrogen | \dots 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 | CH4 | 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 | $\dots N_2$ | 28.1 | 27.5 | 124.0 | 2.45 | 69 | [69] | |
| Hydrogen selenide | e 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 tetrachlori | de CCl ₄ | 153.8 | 44.97 | 556.15 | 2.99 | 460 | 435 | 25 |
| Ammonia | NH3 | 17.1 | 107.6 | 404.0 | 3.02 | 52 | 4 I | II |
| Benzene | C ₆ H ₆ | 78.0 | 47.89 | 561.5 | 3.07 | 239 | 26 3 | -24 |
| Hexamethylene | $C_{6}H_{12}$ | 84.1 | 39.82 | 5 52.95 | 3.08 | 259 | 275 | —16 |
| Diisopropyl | C ₆ H ₁₄ | 86 . I | 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.

EUGENE C. BINGHAM.

TABLE I-Continued.

| TABLE I-Continued. | | | | | | | | | |
|--------------------|------------------------------------|-------------------|------------|---------|--------------|------------|---------|------|--|
| Substance. | Formula. | м. | π atm. | au abs. | α'. | мα'. | Mα'calc | Diff | |
| Pentane | $C_{5}H_{12}$ | 72. I | 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_5C1 | 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 ₄ H ₁₀ C |) 74.1 | 35.61 | 467.4 | 3.29 | 244 | 228 | 16 | |
| Hexane | $C_{6}H_{14}$ | 86. I | 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 ₂ O | 18.0 | 194.6 | 638.0 | 3.80 | 6 8 | 45 | 23 | |
| Ethyl acetate | $C_4H_8O_5$ | 1.88.2 | 37·94 | 523.I | 3.61 | 318 | 265 | 53 | |
| Acetic acid | . C_2H_4O | ₂ 60.0 | 57.11 | 594.6 | 3.85 | 231 | 173 | 58 | |
| Methyl butyrate | $C_{5}H_{10}O$ | 2 102.1 | 34.21 | 554.25 | 3.66 | 374 | 311 | 63 | |
| Octane | $ C_8 H_{18}$ | 114.1 | 24.70 | 569.2 | 3.69 | 421 | 370 | 51 | |
| Methyl alcohol | CH4O | 32.0 | 78.63 | 513.0 | 4.22 | 135 | 90 | 45 | |
| Ethyl alcohol | $ C_2 H_6 O$ | 46.0 | 62.76 | 516.6 | 4.50 | 207 | 136 | 71 | |
| Propyl alcohol | C ₃ H ₈ C |) 60.1 | 50.16 | 536.7 | 4.45 | 267 | 182 | 85 | |
| Isobutyl alcohol | $ C_4 H_{10}$ | D 74.I | 48.27 | 538.0 | 4.87 | 361 | 228 | 133 | |

TABLE II.

| formula. | М. | π atm. | au abs. | α'. | мα'. 1 | Mα' calc | . Diff. |
|----------------|--|--|--|--|--|--|--|
| CH_4 | 16.0 | 55.2 | 191.2 | 2.26 | 36 | 50 | <u>-14</u> |
| C_2H_6 | 30.0 | 45.2 | 308.0 | 2.47 | 74 | 95 | 21 |
| C_2H_4 | 28.0 | 53.5 | 282.8 | 2.76 | 77 | 92 | -15 |
| C_3H_8 | 44. I | 44. | 370 | 3.14 | 138 | 141 | - 3 |
| $C_{5}H_{12}$ | 72.1 | 33.03 | 470.2 | 3.21 | 231 | 233 | 2 |
| C_5H_{12} | 7 2. I | 32.92 | 460.8 | 3.22 | 232 | 233 | — 1 |
| C_5H_{10} | 70. I | 33.9 | 464.6 | 3.34 | 234 | 229 | 5 |
| C_6H_6 | 78.0 | 47.89 | 561.5 | 3.07 | 239 | 263 | -24 |
| $C_{6}H_{12}$ | 84. I | 39.82 | 552.95 | 3.08 | 259 | 275 | —16 |
| $C_{6}H_{14}$ | 86.1 | 29.62 | 507.8 | 3.38 | 291 | 279 | I 2 |
| C_6H_{14} | 86. I | 30.72 | 500.4 | 3. 19 | 275 | 279 | - 4 |
| C_7H_8 | 92.I | 41.6 | 593.6 | 3.22 | 297 | 309 | -12 |
| $C_{7}H_{16}$ | 100.I | 26.86 | 539.9 | 3.66 | 366 | 324 | 42 |
| $C_{8}H_{10}$ | 106.1 | 36.9 | 631.3 | 3.30 | 350 | 355 | — 5 |
| C_8H_{10} | 106.1 | 35.8 | 618.6 | 3.46 | 367 | 355 | 12 |
| $C_{8}H_{10}$ | 106.1 | 35.0 | 617.4 | 3.40 | 361 | 355 | 6 |
| $C_{8}H_{10}$ | 106.1 | 38.1 | 619.4 | 3.36 | 356 | 355 | I |
| $C_{8}H_{18}$ | 114.1 | 24.55 | 549.8 | 3.58 | 408 | 370 | 38 |
| $C_{8}H_{18}$ | 114.1 | 24.70 | 569.2 | 3.69 | 421 | 370 | 51 |
| C_9H_{12} | I 20. I | 33.2 | 640.7 | 3.75 | 450 | 401 | 49 |
| $C_{9}H_{12}$ | 120.1 | 32.3 | 638.6 | 3.50 | 420 | 401 | 19 |
| C_9H_{12} | 120.1 | 32.2 | 635.7 | 3.41 | 410 | 401 | 9 |
| $C_{9}H_{12}$ | 120.1 | 33.2 | 654.2 | 3.60 | 432 | 401 | 31 |
| $C_{10}H_{8}$ | 128.1 | 39.2 | 741.2 | 3.50 | 448 | 435 | 13 |
| $C_{10}H_{14}$ | 134.1 | 28.6 | 675.5 | 3.58 | 480 | 447 | 33 |
| $C_{10}H_{14}$ | 134.1 | 31.1 | 650.1 | 3.54 | 475 | 447 | 28 |
| | ormula. CH_4 C_2H_6 C_2H_6 C_2H_8 C_5H_{12} $C_5C_5C_6H_{14}$ $C_5C_5C_6H_{14}$ C_5H_{16} C_5H_{16} C_5H_{16} C_5H_{16} C_5H_{16} C_5H_{16} C_5H_{16} C_5H_{10} | $\begin{array}{llllllllllllllllllllllllllllllllllll$ | $\begin{array}{llllllllllllllllllllllllllllllllllll$ | $\begin{array}{llllllllllllllllllllllllllllllllllll$ | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | ormula.M. π atm. τ abs. α' .M α' M α' calcCH416.055.2191.22.263650C2H630.045.2308.02.477495C2H428.053.5282.82.767792C3H844.144.3703.14138141C6H1272.133.03470.23.21231233C5H1272.132.92460.83.22232233C5H1070.133.9464.63.34234229C6H678.047.89561.53.07239263CeH1284.139.82552.953.08259275C6H1486.120.72500.43.19275279C7H892.141.6593.63.22297309C7H16100.126.86539.93.66366324C8H10106.135.8618.63.46367355C8H10106.135.0617.43.40361355C8H10106.135.0617.43.40361355C8H10106.135.2640.73.75450401C9H12120.132.2640.73.75450401C9H12120.132.2635.73.41410401C9H12120.132.2635.73.41410401C9H12120.1 </td |

720

| Substance. | Formula. | М. | π atm. | au abs. | α'. | Mα'. | Mα'caic. | 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 |
| | | TAB | LE III. | | | | | - |
| Substance | Formula | M. | πatm | 7 abs | α' | мα′ | Ma ^r calc | Diff. |
| Methylamine | CH-N | 3T.T | 72.0 | 128.0 | 2.27 | 105 | 86 | 10 |
| Dimethylamine | C _a H _a N | 45.T | 56.0 | 436.0 | 3.40 | 157 | 122 | -7 |
| Trimethylamine | C.H.N | 50.1 | 41.0 | 122.5 | 2.07 | 181 | 178 | -3 |
| Ethylamine | C.H.N | 45.T | 66.0 | 450.0 | 2.70 | 101 | 122 | 20 |
| Diethylamine | C.HN | 73.T | 30.3 | 401.0 | 2.62 | 102 | 222 | |
| Triethylamine | C.HN | 101.2 | 20.0 | 5220 | 2 51 | 19- | 215 | 31 |
| Propylamine | C.H.N | 50 1 | 50.0 | 401.0 | 2 67 | 200 | 5+5 1#8 | 40 |
| Dipropylamine | C.H.N | | 21.0 | 550.0 | 2.04 | 21/ | 215 | 39 |
| Aniline | C.H.N | 07.1 | 52.25 | 608 7 | 3.94 9.65 | 390 | 313 | 03 |
| Dimethylaniline | CH.N | 93·* | 22.33 | 687 15 | 3.03 | 340 | 300 | 40 - 8 |
| Dimethylorthotolui. | C 81111 | 121.1 | 33.0 | 007.45 | 3./1 | 449 | 391 | 50 |
| dine | CHN | T 2 5 T | 10.8 | 667 8 | a 6- | 10.0 | 4.0- | -6 |
| Propionitrile | CHN | 133.1 | 30.0 | 507.0 558 7 | 3.05 | 493 | 437 | 50 |
| Propionitrile | CHN | 55.1 60 T | 41.3 | 550.7 | 3.55 | 190 | 170 | 20 |
| Conversional Conversion | CH N | 09.1 | 3/.4 | 502.1 | 3.07 | 254 | 210 | 30 |
| Capionitrile | $C \mathbf{H} \mathbf{N}$ | 97.1 | 32.15 | 600.0 | 3.77 | 300 | 307 | 59 |
| Nitroug owide | NO | 103.1 | 41.0 | 099.0 | 3.59 | 370 | 338 | 32 |
| Nitrous Oxide | $M_2 \cup$ | 44.1 | 74.0 | 308.9 | 2.00 | 120 | 110 | 10 |
| Nitric oxide | NO | 30.0 | 71.2 | 179.5 | 4.30 | 131 | 75 | 56 |
| | | | | | | | | |
| | | Tabi | E IV. | | | | | |
| Substance. | Formula. | Таві м. | æ IV. πatm. | au abs. | α'. | мα'. | Mα' caic. | Diff. |
| Substance. Methyl chloride | Formula. CH3Cl | Таві м. 50.5 | Æ IV. π atm. 73.0 | τ abs. 414.5 | α′. 2.99 | мα'. 151 | мα' caic. 146 | Diff. 5 |
| Substance. Methyl chloride Chloroform | Formula. CH ₃ Cl CHCl ₃ | Таві м. 50.5 119.4 | .Ε IV. ^π atm. 73.0 54.9 | τ abs. 414.5 533.0 | α'. 2.99 3.17 | мα'. 151 379 | Mα' caic. 146 338 | Diff. 5 41 |
| Substance. Methyl chloride Chloroform Carbon tetrachloride | Formula. CH ₃ Cl CHCl ₃ CCl ₄ | Таві м. 50.5 119.4 153.8 | π atm. 73.0 54.9 44.97 | τ abs. 414.5 533.0 556.15 | α'. 2.99 3.17 2.99 | мα'. 151 379 460 | mα' caic. 146 338 435 | Diff. 5 41 25 |
| Substance. Methyl chloride Chloroform Carbon tetrachloride Ethylene chloride | Formula. CH_3Cl $CHCl_3$ CCl_4 $C_2H_4Cl_2$ | Tabi M. 50.5 119.4 153.8 98.9 | E IV. π atm. 73.0 54.9 44.97 53.0 | τ abs. 414.5 533.0 556.15 561.4 | α'. 2.99 3.17 2.99 3.28 | Mα'. 151 379 460 324 | Mα' caic. 146 338 435 288 | Diff. 5 41 25 36 |
| Substance. Methyl chloride Chloroform Carbon tetrachloride Ethylene chloride Ethylidene chloride. | Formula. CH_3Cl $CHCl_3$ CCl_4 $C_2H_4Cl_2$ $C_2H_4Cl_2$ | TABI M. 50.5 119.4 153.8 98.9 98.9 | E IV. π atm. 73.0 54.9 44.97 53.0 52.4 | τ abs. 414.5 533.0 556.15 561.4 528.0 | α'. 2.99 3.17 2.99 3.28 3.19 | Mα'. 151 379 460 324 316 | Mα ['] caic. 146 338 435 288 288 | Diff. 5 41 25 36 28 |
| Substance. Methyl chloride Chloroform Carbon tetrachloride Ethylene chloride Ethylidene chloride | Formula. CH ₃ Cl CHCl ₃ CCl ₄ C ₂ H ₄ Cl ₂ C ₂ H ₄ Cl ₂ C ₈ H ₇ Cl | TABI M. 50.5 119.4 153.8 98.9 98.9 78.5 | E IV. π atm. 73.0 54.9 44.97 53.0 52.4 49.0 | τ abs. 414.5 533.0 556.15 561.4 528.0 494.0 | α'. 2.99 3.17 2.99 3.28 3.19 3.43 | Mα ['] . 151 379 460 324 316 269 | Mα' calc. 146 338 435 288 288 288 238 | Diff. 5 41 25 36 28 31 |
| Substance. Methyl chloride Chloroform Carbon tetrachloride Ethylene chloride Ethylidene chloride. Propyl chloride Phenyl chloride | Formula. CH ₃ Cl CHCl ₃ CCl ₄ C ₂ H ₄ Cl ₂ C ₂ H ₄ Cl ₂ C ₃ H ₇ Cl C ₆ H ₅ Cl | TABI M. 50.5 119.4 153.8 98.9 98.9 78.5 112.5 | $\begin{array}{c} \mathbf{F} \mathrm{IV.} \\ \pi \text{ atm.} \\ 73.0 \\ 54.9 \\ 44.97 \\ 53.0 \\ 52.4 \\ 49.0 \\ 44.62 \end{array}$ | τ abs. 414.5 533.0 556.15 561.4 528.0 494.0 633.0 | α'. 2.99 3.17 2.99 3.28 3.19 3.43 3.18 | Mα'. 151 379 460 324 316 269 358 | Mα' calc. 146 338 435 288 288 288 238 360 | Diff. 5 41 25 36 28 31 - 2 |
| Substance. Methyl chloride Chloroform Carbon tetrachloride Ethylene chloride Ethylidene chloride. Propyl chloride Germanium tetra- | Formula. CH_3Cl CCl_4 $C_2H_4Cl_2$ $C_2H_4Cl_2$ C_3H_7Cl C_6H_5Cl | TABI M. 50.5 119.4 153.8 98.9 98.9 98.9 78.5 112.5 | F IV. π atm. 73.0 54.9 44.97 53.0 52.4 49.0 44.62 | τ abs. 414.5 533.0 556.15 561.4 528.0 494.0 633.0 | α'. 2.99 3.17 2.99 3.28 3.19 3.43 3.18 | Mα'. 151 379 460 324 316 269 358 | Mα' calc. 146 338 435 288 288 288 238 360 | Diff. 5 41 25 36 28 31 — 2 |
| Substance. Methyl chloride Chloroform Carbon tetrachloride Ethylene chloride Ethylidene chloride. Propyl chloride Phenyl chloride Germanium tetra- chloride | Formula. CH ₃ C1 CHCl ₃ CCl ₄ C ₂ H ₄ Cl ₂ C ₂ H ₄ Cl ₂ C ₃ H ₇ C1 C ₆ H ₅ C1 GeCl ₄ | TABI M. 50.5 119.4 153.8 98.9 98.9 78.5 112.5 214.3 | F IV. π atm. 73.0 54.9 44.97 53.0 52.4 49.0 44.62 38.0 | τ abs. 414.5 533.0 556.15 561.4 528.0 494.0 633.0 549.9 | α'. 2.99 3.17 2.99 3.28 3.19 3.43 3.18 3.26 | Mα'. 151 379 460 324 316 269 358 699 | Mα' calc. 146 338 435 288 288 288 238 360 [699] | Diff. 5 41 25 36 28 31 — 2 |
| Substance. Methyl chloride Chloroform Carbon tetrachloride Ethylene chloride Ethylidene chloride Phenyl chloride Germanium tetra- chloride Ethylene bromide | Formula. CH ₃ C1 CHCl ₃ CCl ₄ C ₂ H ₄ Cl ₂ C ₂ H ₄ Cl ₂ C ₃ H ₇ C1 C ₆ H ₅ C1 GeCl ₄ C ₂ H ₄ Br ₂ | TABI M. 50.5 119.4 153.8 98.9 98.9 78.5 112.5 214.3 188.0 | F IV. π atm. 73.0 54.9 44.97 53.0 52.4 49.0 44.62 38.0 70.6 | τ abs. 414.5 533.0 556.15 561.4 528.0 494.0 633.0 549.9 582.8 | α'. 2.99 3.17 2.99 3.28 3.19 3.43 3.18 3.26 5.05 | Mα'. 151 379 460 324 316 269 358 699 950 | Mα ⁷ calc. 146 338 435 288 288 238 360 [699] 735 | Diff. 5 41 25 36 28 31 - 2 215 |
| Substance. Methyl chloride Chloroform Carbon tetrachloride Ethylene chloride Ethylidene chloride. Propyl chloride Germanium tetra- chloride Ethylene bromide | Formula. CH ₃ C1 CHCl ₃ CCl ₄ C ₂ H ₄ Cl ₂ C ₂ H ₄ Cl ₂ C ₃ H ₇ C1 C ₆ H ₅ C1 GeCl ₄ C ₂ H ₄ Br ₂ C ₄ H ₄ S | TABI M. 50.5 119.4 153.8 98.9 98.9 78.5 112.5 214.3 188.0 84.1 | F IV. π atm. 73.0 54.9 44.97 53.0 52.4 49.0 44.62 38.0 70.6 47.7 | τ abs. 414.5 533.0 556.15 561.4 528.0 494.0 633.0 549.9 582.8 590.3 | α'. 2.99 3.17 2.99 3.28 3.19 3.43 3.18 3.26 5.05 2.67 | Mα'. 151 379 460 324 316 269 358 699 950 225 | Mα' calc. 146 338 435 288 288 288 238 360 [699] 735 261 | Diff. 5 41 25 36 28 31 - 2 215 -36 |
| Substance. Methyl chloride Chloroform Carbon tetrachloride Ethylene chloride Ethylidene chloride. Propyl chloride Germanium tetra- chloride Ethylene bromide | Formula. CH ₃ Cl CHCl ₃ CCl ₄ C ₂ H ₄ Cl ₂ C ₂ H ₄ Cl ₂ C ₃ H ₇ Cl C ₆ H ₅ Cl GeCl ₄ C ₂ H ₄ Br ₂ C ₄ H ₄ S | TABI M. 50.5 119.4 153.8 98.9 98.9 78.5 112.5 214.3 188.0 84.1 TAB | μ IV. π atm. 73.0 54.9 44.97 53.0 52.4 49.0 44.62 38.0 70.6 47.7 LE V | τ abs. 414.5 533.0 556.15 561.4 528.0 494.0 633.0 549.9 582.8 590.3 | α'. 2.99 3.17 2.99 3.28 3.19 3.43 3.18 3.26 5.05 2.67 | Mα'. 151 379 460 324 316 269 358 699 950 225 | Mα' calc. 146 338 435 288 288 288 238 360 [699] 735 261 | Diff. 5 41 25 36 28 31 - 2 215 -36 |
| Substance. Methyl chloride Chloroform Carbon tetrachloride Ethylene chloride Ethylidene chloride Phenyl chloride Germanium tetra- chloride Ethylene bromide Thiophene | Formula. $CH_{3}Cl$ $CH_{2}l_{3}$ Ccl_{4} $C_{2}H_{4}Cl_{2}$ $C_{3}H_{7}Cl$ $C_{6}H_{5}Cl$ GeCl ₄ $C_{2}H_{4}Br_{2}$ $C_{4}H_{4}S$ | TABI M. 50.5 119.4 153.8 98.9 98.9 78.5 112.5 214.3 188.0 84.1 TAB | μ IV. π atm. 73.0 54.9 44.97 53.0 52.4 49.0 44.62 38.0 70.6 47.7 LE V. π atm | τ abs. 414.5 533.0 556.15 561.4 528.0 494.0 633.0 549.9 582.8 590.3 τ abs | α'. 2.99 3.17 2.99 3.28 3.19 3.43 3.18 3.26 5.05 2.67 | Mα ['] . 151 379 460 324 316 269 358 699 950 225 | Mα' calc. 146 338 435 288 288 288 238 360 [699] 735 261 | Diff. 5 41 25 36 28 31 - 2 215 -36 |
| Substance. Methyl chloride Chloroform Carbon tetrachloride Ethylene chloride Ethylidene chloride Phenyl chloride Germanium tetra- chloride Ethylene bromide Substance. Methyl formate | Formula. CH_3Cl CH_2Cl_3 Ccl_4 $C_2H_4Cl_2$ $C_2H_4Cl_2$ C_3H_7Cl C_6H_5Cl GeCl ₄ $C_2H_4Br_2$ C_4H_4S Formula. $C_2H_4O_2$ | TABI M. 50.5 119.4 153.8 98.9 98.9 78.5 112.5 214.3 188.0 84.1 TAB M. 60.0 | E IV. π atm. 73.0 54.9 44.97 53.0 52.4 49.0 44.62 38.0 70.6 47.7 LE V. π atm. 59.25 | τ abs. 414.5 533.0 556.15 561.4 528.0 494.0 633.0 549.9 582.8 590.3 τ abs. 487.0 | α'. 2.99 3.17 2.99 3.28 3.19 3.43 3.18 3.26 5.05 2.67 α'. 3.22 | Mα ['] . 151 379 460 324 316 269 358 699 950 225 Mα ['] . | Mα' calc. 146 338 435 288 288 288 238 360 [699] 735 261 Μα' calc. | Diff. 5 41 25 36 28 31 - 2 215 -36 Diff. |
| Substance. Methyl chloride Chloroform Carbon tetrachloride Ethylene chloride Ethylidene chloride Phenyl chloride Germanium tetra- chloride Ethylene bromide Substance. Methyl formate Ethyl formate | Formula. $CH_{3}Cl$ $CH_{2}l_{3}$ Ccl_{4} $C_{2}H_{4}Cl_{2}$ $C_{3}H_{7}Cl$ $C_{6}H_{5}Cl$ GeCl ₄ $C_{2}H_{4}Br_{2}$ $C_{4}H_{4}S$ Formula. $C_{2}H_{4}O_{2}$ $C_{4}H_{4}O_{2}$ | TABI M. 50.5 119.4 153.8 98.9 98.9 78.5 112.5 214.3 188.0 84.1 TAB M. 60.0 74.1 | E IV. π atm. 73.0 54.9 44.97 53.0 52.4 49.0 44.62 38.0 70.6 47.7 LE V. π atm. 59.35 46.82 | τ abs. 414.5 533.0 556.15 561.4 528.0 494.0 633.0 549.9 582.8 590.3 τ abs. 487.0 508.2 | α' . 2.99 3.17 2.99 3.28 3.19 3.43 3.18 3.26 5.05 2.67 α' . 3.22 2.20 | Mα'. 151 379 460 324 316 269 358 699 950 225 Mα'. 193 244 | Mα' calc. 146 338 435 288 288 288 238 360 [699] 735 261 Mα' calc. 173 270 | Diff. 5 41 25 36 28 31 - 2 215 - 36 215 - 36 Diff. 20 |
| Substance. Methyl chloride Chloroform Carbon tetrachloride Ethylene chloride Ethylidene chloride Propyl chloride Germanium tetra- chloride Ethylene bromide Substance. Methyl formate Ethyl formate | Formula. $CH_{3}Cl$ $CH_{2}l_{3}$ Ccl_{4} $C_{2}H_{4}Cl_{2}$ $C_{2}H_{4}Cl_{2}$ $C_{3}H_{7}Cl$ $C_{6}H_{5}Cl$ GeCl ₄ $C_{2}H_{4}Br_{2}$ $C_{4}H_{4}S$ Formula. $C_{2}H_{4}O_{2}$ $C_{3}H_{6}O_{2}$ $C_{7}H_{6}O_{2}$ | TABI M. 50.5 119.4 153.8 98.9 98.9 78.5 112.5 214.3 188.0 84.1 TAB M. 60.0 74.1 88.1 | E IV. π atm. 73.0 54.9 44.97 53.0 52.4 49.0 44.62 38.0 70.6 47.7 LE V. π atm. 59.35 46.83 40.05 40. | au abs. 414.5 533.0 556.15 561.4 528.0 494.0 633.0 549.9 582.8 590.3 au abs. 487.0 508.3 517.8 | $\alpha'.$ 2.99 3.17 2.99 3.28 3.19 3.43 3.18 3.26 5.05 2.67 $\alpha'.$ 3.22 3.30 2.42 | Mα'. 151 379 460 324 316 269 358 699 950 225 Mα'. 193 244 202 | $M\alpha'_{calc.}$ 146 338 435 288 288 288 238 360 [699] 735 261 $M\alpha'_{calc.}$ 173 219 267 | Diff. 5 41 25 36 28 31 - 2 215 - 36 215 - 36 Diff. 205 25 2 |
| Substance. Methyl chloride Chloroform Carbon tetrachloride Ethylene chloride Ethylidene chloride Phenyl chloride Germanium tetra- chloride Ethylene bromide Substance. Methyl formate Propyl formate | Formula. $CH_{3}Cl$ CCl_{4} $C_{2}H_{4}Cl_{2}$ $C_{2}H_{4}Cl_{2}$ $C_{3}H_{7}Cl$ $C_{6}H_{5}Cl$ GeCl ₄ $C_{2}H_{4}Br_{2}$ $C_{4}H_{4}S$ Formula. $C_{2}H_{4}O_{2}$ $C_{3}H_{6}O_{2}$ $C_{4}H_{5}O_{2}$ | TABI M. 50.5 119.4 153.8 98.9 98.9 78.5 112.5 214.3 188.0 84.1 TAB M. 60.0 74.1 88.1 16.1 | E IV. π atm. 73.0 54.9 44.97 53.0 52.4 49.0 44.62 38.0 70.6 47.7 LE V. π atm. 59.35 46.83 40.05 24.15 24.15 25.25 25. | au abs. 414.5 533.0 556.15 561.4 528.0 494.0 633.0 549.9 582.8 590.3 au abs. 487.0 508.3 537.85 575.6 | α' . 2.99 3.17 2.99 3.28 3.19 3.43 3.18 3.26 5.05 2.67 α' . 3.22 3.30 3.420 | Mα'. 151 379 460 324 316 269 358 699 950 225 Mα'. 193 244 302 488 | $M\alpha'$ calc. 146 338 435 288 288 288 238 360 [699] 735 261 $M\alpha'$ calc. 173 219 265 | Diff. 5 4I 25 36 28 31 - 2 215 - 36 Diff. 20 25 37 |
| Substance. Methyl chloride Chloroform Carbon tetrachloride Ethylene chloride Ethylidene chloride Phenyl chloride Germanium tetra- chloride Ethylene bromide Thiophene Substance. Methyl formate Amyl formate Methyl acetate | Formula. $CH_{3}Cl$ $CH_{2}l_{3}$ CCl_{4} $C_{2}H_{4}Cl_{2}$ $C_{2}H_{4}Cl_{2}$ $C_{3}H_{7}Cl$ $C_{6}H_{5}Cl$ GeCl ₄ $C_{2}H_{4}Br_{2}$ $C_{4}H_{4}S$ Formula. $C_{2}H_{4}O_{2}$ $C_{3}H_{6}O_{2}$ $C_{6}H_{1}O_{2}$ | TABI M. 50.5 119.4 153.8 98.9 98.9 78.5 112.5 214.3 188.0 84.1 TAB M. 60.0 74.1 88.1 116.1 116.1 174.4 | E IV. π atm. 73.0 54.9 44.97 53.0 52.4 49.0 44.62 38.0 70.6 47.7 LE V. π atm. 59.35 46.83 40.05 34.12 26.20 | au abs. 414.5 533.0 556.15 561.4 528.0 494.0 633.0 549.9 582.8 590.3 au abs. 487.0 508.3 537.85 575.6 | α' . 2.99 3.17 2.99 3.28 3.19 3.43 3.18 3.26 5.05 2.67 α' . 3.22 3.30 3.420 3.43 | Mα'. 151 379 460 324 316 269 358 699 950 225 Mα'. 193 244 302 482 257 | $M\alpha'$ calc. 146 338 435 288 288 238 360 [699] 735 261 $M\alpha'$ calc. 173 219 265 356 | Diff. 5 4I 25 36 28 31 - 2 215 - 36 Diff. 20 25 37 1322 2 |
| Substance. Methyl chloride Chloroform Carbon tetrachloride Ethylene chloride Ethylidene chloride Phenyl chloride Germanium tetra- chloride Ethylene bromide Substance. Methyl formate Amyl formate Methyl acetate | Formula. CH_3Cl CH_2Cl_3 CCl_4 $C_2H_4Cl_2$ $C_2H_4Cl_2$ C_8H_7Cl C_6H_5Cl GeCl ₄ $C_2H_4Br_2$ C_4H_4S Formula. $C_2H_4O_2$ $C_8H_6O_2$ $C_8H_6O_2$ $C_8H_6O_2$ $C_8H_6O_2$ | TABI M. 50.5 119.4 153.8 98.9 98.9 78.5 112.5 214.3 188.0 84.1 TAB M. 60.0 74.1 88.1 116.1 74.1 88.1 | E IV. π atm. 73.0 54.9 44.97 53.0 52.4 49.0 44.62 38.0 70.6 47.7 LE V. π atm. 59.35 46.83 40.05 34.12 46.29 37.04 | τ abs. 414.5 533.0 556.15 561.4 528.0 494.0 633.0 549.9 582.8 590.3 τ abs. 487.0 508.3 537.85 575.6 506.7 523 T | α' . 2.99 3.17 2.99 3.28 3.19 3.43 3.18 3.26 5.05 2.67 α' . 3.22 3.30 3.43 4.20 3.43 4.20 3.43 | Mα'. 151 379 460 324 316 269 358 699 950 225 Mα'. 193 244 302 488 257 8 | $M\alpha'$ calc. 146 338 435 288 288 288 238 360 [699] 735 261 $M\alpha'$ calc. 173 219 265 356 219 267 | Diff. 5 41 25 36 28 31 - 2 215 - 36 Diff. 20 25 37 132 38 38 37 - 2 - 36 - 36 - 2 - 36 - 36 - 2 - 36 - 37 - 36 - 37 - 37 - 37 - 36 - 37 - 37 - 37 - 36 - 37 - 37 37 - 37 - 3 |
| Substance. Methyl chloride Chloroform Carbon tetrachloride Ethylene chloride Ethylidene chloride. Propyl chloride Germanium tetra- chloride Ethylene bromide Thiophene Substance. Methyl formate Propyl formate Amyl formate Ethyl acetate Ethyl acetate | Formula. CH ₃ Cl CHCl ₃ CCl ₄ C ₂ H ₄ Cl ₂ C ₂ H ₄ Cl ₂ C ₃ H ₇ Cl C ₆ H ₅ Cl GeCl ₄ C ₂ H ₄ Br ₂ C ₄ H ₄ S Formula. C ₂ H ₄ O ₂ C ₄ H ₆ O ₂ C ₄ H ₈ O ₂ | TABI M. 50.5 119.4 153.8 98.9 98.9 78.5 112.5 214.3 188.0 84.1 TAB M. 60.0 74.1 88.1 116.1 74.1 88.1 102.1 | E IV. π atm. 73.0 54.9 44.97 53.0 52.4 49.0 44.62 38.0 70.6 47.7 LE V. π atm. 59.35 46.83 40.05 34.12 46.29 37.94 42.217 | au abs. 414.5 533.0 556.15 561.4 528.0 494.0 633.0 549.9 582.8 590.3 au abs. 487.0 508.3 537.85 575.6 506.7 523.1 | α' . 2.99 3.17 2.99 3.28 3.19 3.43 3.18 3.26 5.05 2.67 α' . 3.22 3.30 3.43 4.20 3.43 4.20 3.47 3.67 | Mα'. 151 379 460 324 316 269 358 699 950 225 Mα'. 193 244 302 488 257 318 280 | $M\alpha'$ calc. 146 338 435 288 288 288 238 360 [699] 735 261 $M\alpha'$ calc. 173 219 265 356 219 265 356 219 265 | Diff. 5 36 28 31 - 2 215 5 36 28 31 - 2 215 5 36 20 25 37 132 38 53 3 |

TABLE II—Continued.

EUGENE C. BINGHAM.

TABLE V-Continued.

| Substance. | Formula. | м. | π atm. | au abs | α'. | мα'. | $M\alpha'_{calc.}$ | 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 | $C_5H_{10}O_2$ | 10 2.1 | 33.17 | 545.9 | 3.71 | 379 | 311 | 68 |
| Methyl butyrate | $C_5H_{10}O_2$ | 102.I | 34.21 | 554.25 | 3.66 | 374 | 311 | 63 |
| Ethyl butyrate | $C_6H_{12}O_2$ | 116.1 | 30.24 | 565.8 | 3.88 | 45 I | 356 | 94 |
| Methyl isobutyrate | $C_5H_{10}O_2$ | I02. I | 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 |
| | | TAB | LE VI. | | | | | |
| Substance. | Formula. | м. | π atm. | au abs. | α'. | мα'. | Mα' calc. | Diff. |
| Methyl ether | C_2H_6O | 46. I | 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.I | 35.61 | 467.4 | 3.29 | 244 | 228 | 16 |
| Acetone | C_3H_6O | 58.o | 6ം.o | 510.5 | 3.53 | 205 | 223 | 18 |
| Methyl alcohol | CH_4O | 32.0 | 78.6 3 | 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 | $C_{3}H_{8}O$ | бо. 1 | 50.16 | 536.7 | 4.45 | 267 | 182 | 85 |
| Isopropyl alcohol | C_3H_8O | 60.1 | 53.I | 507.6 | 4. 9 1 | 295 | 182 | 13 |
| Isobutyl alcohol | $C_4H_{10}O$ | 74.I | 48.27 | 5 3 8.0 | 4.87 | 361 | 228 | 133 |
| Cresol | $C_1 H_8 O$ | 108.1 | 45.0 | 705.0 | 3.9 4 | 426 | 350 | 76 |
| Anisol | $C_7 H_8 O$ | 108.1 | 41.25 | 641.5 | 3.62 | 39 5 | 350 | 45 |
| Water | H_2O | 18.0 | 194.6 | 63 8.0 | 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 | 4 4.0 | 72.9 | 304.35 | 3.15 | 139 | 124 | 15 |
| Sulphur dioxide | SO_2 | 64. I | 78. 9 | 4 2 8.4 | 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 $M\alpha'$.

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, \ldots are the number of atoms of the elements, carbon, hydrogen, oxygen,... respectively in the molecule.

BERLIN, March, 1906.

THE RELATION OF HEAT OF VAPORIZATION TO BOILING-POINT.

BY EUGENE C. BINGHAM. Received March 27, 1906.

TROUTON'S rule states that the quotient of the molecular heat of vaporization divided by the absolute temperature of the boilingpoint 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:

$$\frac{\lambda'}{\Gamma_{o}} = 8.5 \log T_{o},$$

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

7

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