**Table IV. Enthalpy of Solution of $NH_4H_2PO_4$ in 850.0 ml of 10.34*m* HCl and Stoichiometric $H_2O$ at 40°C**

| Wt sample, g | —Corr temp rise, °C | $\Delta H_4$, cal/mol | Δ |
|---|---|---|---|
| 14.90333 | 0.97704 | 5457 | +4 |
| 15.00510 | 0.98473 | 5453 | ±0 |
| 15.02232 | 0.98401 | 5448 | −5 |
| 15.10264 | 0.98916 | 5451 | −2 |
| 15.12050 | 0.99038 | 5447 | −6 |
| 15.15361 | 0.99289 | 5466 | +13 |
| 15.20558 | 0.99578 | 5452 | −1 |
| 15.22108 | 0.99749 | 5451 | −2 |
| | Av, double SD | 5453 | ±4 |

cal (double standard deviation) for Equation 1 at 40°C. This value was adjusted by −1552 ± 2 cal to give −15,675 ± 32 cal for the enthalpy of reaction at 25°C according to the equation

$$\Delta H_R(25°C) = \Delta H_R(40°C) + \int_{313.15}^{298.15} \Delta C_p\, dT \qquad (2)$$

through use of polynomial equations for determining differences between the heat capacities of the products and the reactants. The heat capacity equations were derived from the data of Osborne et al. for water (*6*), of Stephenson and Zettlemoyer for $NH_4H_2PO_4$ (*8*), of Egan et al. for phosphoric acid solutions (*2*), and of Wakefield and Luff for $(NH_4)_3HP_2O_7 \cdot H_2O$ (*9*).

The standard enthalpies of formation of $H_3PO_4(l)$, −302.8 kcal, and $H_3PO_4 \cdot 15H_2O$ (soln), −307.715 kcal (*5*), were used to determine the enthalpy of the reaction

$$H_3PO_4(l) + 15H_2O = H_3PO_4 \cdot 15H_2O \qquad (3)$$

at 25°C, −4.9 kcal. The enthalpy of the reaction

$$H_3PO_4 \cdot 15H_2O + 1.24H_2O = H_3PO_4 \cdot 16.24H_2O \qquad (4)$$

at 25°C, −36.65 cal, was determined from the data of Egan and Luff (*1*). The summation of the enthalpies of reaction of Equations 1, 3, and 4 gives the enthalpy of the reaction

$$(NH_4)_3HP_2O_7 \cdot H_2O(c) + H_3PO_4(l) = 3NH_4H_2PO_4(c) \qquad (5)$$

at 25°C, −20.61 ± 0.1 kcal.

The standard enthalpy of formation of $NH_4H_2PO_4(c)$ is −345.38 kcal/mol (*5*). Substituting the known enthalpies of formation and the enthalpy of reaction of Equation 5 in the equation

$$\Delta H_f°(NH_4)_3HP_2O_7 \cdot H_2O(c) = 3[\Delta H_f°NH_4H_2PO_4(c)] - \Delta H_f°H_3PO_4(l) - \Delta H_R(25°C) \qquad (6)$$

gives −712.7 kcal/mol as the standard enthalpy of formation of $(NH_4)_3HP_2O_7 \cdot H_2O(c)$ at 25°C. An estimate of the uncertainty is not given because it is largely dependent upon the uncertainty of the auxiliary enthalpies of formation taken from ref. *5*.

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# High-Precision Vapor-Pressure Data for Eight Organic Compounds

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**Vapor-pressure data are obtained via comparative ebulliometry for butyronitrile, cyclohexene, 1,3-cyclohexadiene, methylene cyclohexane, di-*n*-propyl ether, and cyclohexanone. In addition, corrected data are presented for capronitrile and lauronitrile. Constants for Antoine and Cox equations, with their statistical uncertainties, are included. The overall average differences between calculated and observed pressures for the new data, expressed as $\Delta p/p$, are $5.6 \times 10^{-5}$ for the Antoine and $4.7 \times 10^{-5}$ for the Cox equation.**

During a study concerning thermodynamics of solution by use of gas-liquid chromatography, the need arose for enthalpy of vaporization data for several compounds. To estimate the enthalpy of vaporization from the Clapeyron equation, we measured the vapor pressures (from about 50°C to slightly above the normal boiling point) of five compounds for which such data are not presently available: cyclohexene, 1,3-cyclohexadiene, methylenecyclohexane, cyclohexanone, and di-*n*-propyl ether. In addition, we are including improved data for butyronitrile and corrected data for lauronitrile and capronitrile.

## Experimental

A comparative ebulliometric technique was used with an apparatus similar to that described by Ambrose (*1*). Instead of four bubble caps, however, only one was used in the present ebulliometer, allowing the use of significantly smaller samples (3 ml) without sacrificing the high precision characteristic of the method.

Two platinum-resistance thermometers were used to measure the temperatures of the liquid-vapor equilibria of water and the liquid under investigation. That used for the latter was calibrated (at Leeds and Northrup) according to IPTS-48. The other was calibrated in this laboratory by use of the triple point of water and several temperatures up to 108°C. The latter was accomplished by using fresh samples of deionized, degassed water in both boilers of

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the ebulliometric apparatus and by using the first thermometer for a reference temperature. (Since the second thermometer is never used outside the calibration range, its narrowness is not a handicap.) For this work both thermometers were converted to IPTS-68, in accord with the discussion of Bedford and Kirby (5). The constants in the equation

$$R_{t'} = R_0\,(1 + At' + Bt'^2) \tag{1}$$

were evaluated by least squares for the second thermometer. The value of unity was treated as a parameter in the analysis and was determined by the fit to be 1.00000002. The average deviation in the calibration data (a total of six points) corresponded to 0.0002°C; the maximum deviation, 0.00034°C.

The precision of the vapor-pressure data was such that correction had to be made for the difference in mass of the vapor columns above the liquid phases in the two boilers for the higher molecular-weight samples. In addition, the liquid surface in the water boiler lay 6 cm below that in the sample boiler; the condenser, through which ice water circulated, was 4 cm longer above the sample than above the water. The last two effects lead to a constant percentage error in the pressure of the sample of 0.00036%. Since the best precision in the present data amounts to 0.003%, these effects can be safely ignored. To correct for the first effect, we used the equation

$$p_s = p_w\left[1 + 2.12 \times 10^{-4}\left(\frac{M_s}{T_s} - \frac{M_w}{T_w}\right)\right] \tag{2}$$

where $p$, $M$, and $T$ represent vapor pressure, molecular weight, and absolute temperature, and the subscripts $s$ and $w$ refer to sample and water, respectively. The constant includes the information that each vapor column is 18 cm high.

The vapor pressure of the water ($p_w$) is calculated from the temperature of the vapor-liquid equilibrium by use of a Chebyshev polynomial (4) with constants determined by Ambrose and Sprake (3).

The resistances of both thermometers at the triple point of water were measured during the course of the work; the sample thermometer exhibited a resistance 0.0002 ohm higher than its original value and the other, 0.0001 ohm higher (0.0001 ohm corresponds to 0.001°).

The coils of the thermostated Mueller bridge used for resistance measurements were also recalibrated by use of a Leeds and Northrup standard resistance of 10.0100 ohms. In no case was the total correction to a bridge reading greater than 0.0001 ohm different from the original calibration values received with the instrument four years ago. The new corrections were used for this work.

Subsequent to an earlier publication from this laboratory (7), it was pointed out (2) that the Chebyshev constants used therein were based on IPTS-68, whereas the thermometer had been calibrated according to IPTS-48. This leads to significant, though small, errors in the data for capronitrile and lauronitrile presented in that paper. (The remaining vapor-pressure data published in ref. 7, for which manometers were used, are consistent but based on IPTS-48.) Consequently, we include here corrected data for these two compounds, based on IPTS-68. In addition, we have repeated the measurements for butyronitrile by use of the comparative ebulliometric apparatus.

Recent suggestions in the literature give rise to the possibility of further changes in the practical temperature scale (6). To preserve the value of good data measured on a practical scale, provision should be made for ready conversion from one scale to another. Thus, we include in Table I values of the characteristic constants for the thermometers used in this work.

In the event that the vapor pressure-temperature relationship used herein for water should prove unsatisfactory, the temperature of the water equilibrium is included with the presentation of the temperature and pressure in Table II for each sample.

All compounds on which new measurements were made were obtained from ChemSampCo (Columbus, Ohio) except cyclohexene, which was from Eastman. Butyronitrile and methylenecyclohexene did not require purification; the remainder were distilled on a Teflon spinning band column. All were better than 99.9% pure by gas-liquid chromatography and were dried over a molecular sieve before use. Helium was used to apply the external pressure to the boiling liquids.

## Results

The results are presented in Table II. Tables III and IV give the values of the Antoine and Cox constants, respectively, for the data in Table II, as well as the temperature range of the data, average deviations in pressure, and the normal boiling points of the compounds studied. Evaluation of the constants was accomplished by the iterative approach to rigorous least-squares analysis described by Wentworth (9). The standard deviation in temperature was taken to be 0.001, and that in pressure was calculated from the expression

$$\sigma_p = \left[\left(\frac{dp}{dT}\right)_w^2 + \left(\frac{dp}{dT}\right)_s\right]^{1/2}\sigma_T \tag{3}$$

where $\sigma$ represents standard deviation, and $w$ and $s$ refer to water and sample, respectively. Weighing the data was accomplished following the paper of Wentworth (9).

## Discussion

One of the most important uses of accurate vapor-pressure data is in the estimation of enthalpies of vaporization or, if calorimetric values are available, evaluation of second-virial coefficients for the vapors in question. Both involve the derivative of log $p$ with respect to $T$:

$$\left(\frac{d\log p}{dT}\right)_{\text{Antoine}} = \frac{B}{(C+t)^2} \tag{4}$$

$$\left(\frac{d\log p}{dT}\right)_{\text{Cox}} = \left[\frac{T_{\text{bp}}}{T^2} + 2.303\left(1 - \frac{T_{\text{bp}}}{T^2}\right)(b + 2\,cT)\right]\cdot 10^{(a+b+cT^2)} \tag{5}$$

These expressions point out one of the reasons for the relative popularity of the Antoine equation. It is of interest to compare the precision of enthalpies of vaporization derived from these two equations. To this end, we have calculated the standard deviation of the enthalpies of vaporization at the boiling point and at a temperature near the low end of the experimental data from the elements of the variance-covariance matrices produced in fitting the data. For both equations the statistical uncertainty averages 0.5 cal/mol and is never greater than 1.1 cal/mol. Since the error introduced through second-virial coefficients in the Clapeyron equation is probably not

**Table I. Thermometer Constants**

|  | $R_o$ | $\alpha_{68}$ | $\delta_{68}$ |
|---|---|---|---|
| Sample thermometer | 25.5404 | 0.003926394 | 1.496947 |
| Water thermometer | 25.5412 | 0.003926841 | 1.500461 |

**Table II. Vapor-Pressure Data**

| Butyronitrile | | | 1,3-Cyclohexadiene | | | Methylene cyclohexane | | | Di-*n*-propyl ether | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $t_w$, °C | $t_s$, °C | $p_s$, kPa | $t_w$, °C | $t_s$, °C | $p_s$, kPa | $t_w$, °C | $t_s$, °C | $p_s$, kPa | $t_w$, °C | $t_s$, °C | $p_s$, kPa |
| 52.310 | 59.807 | 13.831 | 59.464 | 34.185 | 19.444 | 63.374 | 58.645 | 23.240 | 55.789 | 39.703 | 16.358 |
| 57.229 | 65.615 | 17.513 | 64.718 | 39.995 | 24.711 | 68.715 | 65.013 | 29.486 | 61.361 | 45.857 | 21.223 |
| 62.298 | 71.638 | 22.151 | 69.336 | 45.146 | 30.293 | 73.249 | 70.444 | 35.827 | 66.669 | 51.773 | 26.953 |
| 66.802 | 77.023 | 27.111 | 74.272 | 50.687 | 37.406 | 78.447 | 76.742 | 44.476 | 71.984 | 57.749 | 33.952 |
| 72.269 | 83.599 | 34.366 | 78.843 | 55.860 | 45.201 | 83.782 | 83.247 | 55.114 | 76.849 | 63.263 | 41.649 |
| 77.117 | 89.462 | 42.109 | 79.259 | 56.332 | 45.973 | 94.186 | 96.128 | 82.034 | 82.132 | 69.298 | 51.617 |
| 82.501 | 96.022 | 52.382 | 83.990 | 61.740 | 55.567 | 99.466 | 102.755 | 99.414 | 87.254 | 75.199 | 63.121 |
| 87.606 | 102.279 | 63.984 | 89.626 | 68.233 | 69.131 | 103.702 | 108.117 | 115.468 | 89.614 | 77.936 | 69.101 |
| 93.198 | 109.175 | 79.081 | 94.628 | 74.045 | 83.383 | 108.015 | 113.619 | 133.958 | 92.764 | 81.601 | 77.811 |
| 98.417 | 115.651 | 95.737 | 99.142 | 79.332 | 98.263 | | | | 95.004 | 84.221 | 84.548 |
| 103.373 | 121.838 | 114.148 | 104.042 | 85.113 | 116.841 | | | | 100.778 | 91.016 | 104.174 |
| 108.055 | 127.707 | 134.135 | 108.287 | 90.160 | 135.198 | | | | 106.810 | 98.183 | 128.564 |
| Cyclohexene | | | Cyclohexanone | | | Capronitrile | | | Lauronitrile | | |
| 59.947 | 36.875 | 19.885 | 50.612 | 89.628 | 12.725 | 50.799 | 98.079 | 12.843 | 30.682 | 167.746 | 4.4151 |
| 65.930 | 43.560 | 26.084 | 54.701 | 94.896 | 15.528 | 53.729 | 101.861 | 14.818 | 38.171 | 178.991 | 6.6921 |
| 71.453 | 49.795 | 33.189 | 59.255 | 100.807 | 19.257 | 60.560 | 110.711 | 20.455 | 45.585 | 190.226 | 9.8833 |
| 76.707 | 55.785 | 41.404 | 64.507 | 107.664 | 24.477 | 69.081 | 121.896 | 29.960 | 49.343 | 195.963 | 11.949 |
| 82.582 | 62.537 | 52.551 | 69.552 | 114.303 | 30.580 | 74.855 | 129.534 | 38.332 | 53.230 | 201.926 | 14.465 |
| 87.993 | 68.815 | 64.943 | 73.635 | 119.712 | 36.416 | 81.883 | 138.897 | 51.106 | 61.957 | 215.426 | 21.810 |
| 93.580 | 75.354 | 80.213 | 77.814 | 125.282 | 43.337 | 85.316 | 143.510 | 58.538 | 68.678 | 225.921 | 29.438 |
| 98.425 | 81.075 | 95.764 | 81.826 | 130.659 | 50.990 | 94.495 | 155.936 | 82.975 | 73.722 | 233.873 | 36.550 |
| 102.658 | 86.112 | 111.325 | 85.620 | 135.774 | 59.239 | 99.285 | 162.487 | 98.770 | 78.002 | 240.657 | 43.673 |
| 107.053 | 91.378 | 129.633 | 90.022 | 141.742 | 70.181 | 103.669 | 168.510 | 115.335 | 83.216 | 248.970 | 53.893 |
| | | | 93.054 | 145.880 | 78.656 | | | | 87.770 | 256.297 | 64.392 |
| | | | 97.458 | 151.916 | 92.474 | | | | 92.318 | 263.605 | 76.526 |
| | | | 97.493 | 151.969 | 92.593 | | | | 97.218 | 271.578 | 91.674 |
| | | | 101.081 | 156.917 | 105.300 | | | | 103.684 | 282.147 | 115.399 |
| | | | 101.112 | 156.966 | 105.417 | | | | | | |
| | | | 107.454 | 165.769 | 131.422 | | | | | | |

**Table III. Antoine Constants**[a]

| Compound | Temp range, °C | $A$ | $B$ | $C$ | $T_{bp}$, K | Av $\frac{\Delta p}{p} \times 10^5$ |
|---|---|---|---|---|---|---|
| Butyronitrile | 59.8–127.7 | 6.129067 ± 0.000400 | 1452.076 ± 0.804 | 224.1855 ± 0.0277 | 390.770 | 4.1 |
| 1,3-Cyclohexadiene | 34.2–90.2 | 5.865445 ± 0.000481 | 1205.995 ± 0.866 | 222.3226 ± 0.1020 | 353.489 | 6.7 |
| Methylenecyclohexane | 58.6–113.6 | 5.803367 ± 0.001935 | 1253.192 ± 1.171 | 216.0562 ± 0.1409 | 376.578 | 5.8 |
| Di-*n*-propyl ether | 39.7–98.2 | 5.894812 ± 0.000458 | 1227.468 ± 0.824 | 215.7007 ± 0.0950 | 363.246 | 3.1 |
| Cyclohexene | 36.9–91.4 | 5.872420 ± 0.001757 | 1221.899 ± 1.011 | 223.1720 ± 0.1186 | 356.095 | 5.9 |
| Cyclohexanone | 89.6–165.8 | 5.978401 ± 0.000987 | 1495.511 ± 0.666 | 209.5517 ± 0.0747 | 428.572 | 8.0 |
| Capronitrile | 98.1–168.5 | 6.071220 ± 0.001304 | 1553.811 ± 0.888 | 207.3386 ± 0.0968 | 436.613 | 15 |
| Lauronitrile | 167.7–282.1 | 6.081293 ± 0.000592 | 1859.981 ± 0.464 | 166.6944 ± 0.0486 | 549.258 | 21 |

[a] $\log p\ (\text{cm Hg}) = A - \frac{B}{C + t}$. To convert to kPa, add 0.124903 to $A$.

**Table IV. Cox Constants**[a]

| Compound | $a$ | $-b \times 10^3$ | $c \times 10^6$ | $T_{bp}$, K | Av $\frac{\Delta p}{p} \times 10^5$ |
|---|---|---|---|---|---|
| Butyronitrile | 0.846124 ± 0.00317 | 0.667751 ± 0.0178 | 0.662990 ± 0.0250 | 390.7717 ± 0.00068 | 2.5 |
| 1,3-Cyclohexadiene | 0.845439 ± 0.00416 | 0.804445 ± 0.0256 | 0.854257 ± 0.0391 | 353.4899 ± 0.00065 | 5.5 |
| Methylenecyclohexane | 0.846896 ± 0.00550 | 0.762546 ± 0.0314 | 0.741997 ± 0.0448 | 376.5779 ± 0.00073 | 6.3 |
| Di-*n*-propyl ether | 0.866715 ± 0.00375 | 0.812825 ± 0.0226 | 0.809693 ± 0.0339 | 363.2462 ± 0.00061 | 3.2 |
| Cyclohexene | 0.833958 ± 0.00485 | 0.742586 ± 0.0130 | 0.767278 ± 0.0450 | 356.0954 ± 0.00065 | 6.6 |
| Cyclohexanone | 0.852046 ± 0.00340 | 0.612660 ± 0.0175 | 0.504661 ± 0.0225 | 428.5716 ± 0.00069 | 4.0 |
| Capronitrile | 0.863202 ± 0.00362 | 0.597309 ± 0.0185 | 0.475389 ± 0.0236 | 436.6137 ± 0.00072 | 17 |
| Lauronitrile | 0.984965 ± 0.00110 | 0.792482 ± 0.00465 | 0.553941 ± 0.00488 | 549.2613 ± 0.00079 | 9.7 |

[a] $\log p\ (\text{atm}) = A'\left(1 - \frac{T_{bp}}{T}\right)$, where $\log A' = (a + bT + cT^2)$. $T_{bp}$ was treated as a parameter in fitting the data. To convert atm to kPa, multiply by 101.325.

smaller than this, either equation may be used when an enthalpy of vaporization is to be estimated from vapor pressures within the range of experimental data.

However, if one calculates the enthalpy of vaporization at 25°C, there is a real discrepancy between the two equations under discussion, which increases with the length of extrapolation below the experimental data. For example, the difference varies from 4 cal/mol for 1,3-cyclohexadiene to 2500 cal/mol for lauronitrile. Scott (*8*) pointed out that the Cox equation is to be preferred when such an extrapolation becomes necessary, since it behaves properly as temperature decreases, an advantage the Antoine equation does not share.

### Conclusions

Accurate vapor-pressure data have been measured and fitted to Antoine and Cox equations for eight compounds. Within the range of the data, there is no clear advantage to either equation. The statistical uncertainty in enthalpies of vaporization derived from them by use of the Clausius-Clapeyron equation is of the order of 1 cal/mol.

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# Vapor Pressures of Aqueous Solutions of Beryllium Sulfate

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**Water vapor pressures over saturated, aqueous $BeSO_4$ solutions were measured with a differential mercury manometer at 25–93°C for $BeSO_4 \cdot 4H_2O$ as solid phase and at 90–110°C for $BeSO_4 \cdot 2H_2O$ as solid phase. The transition temperature of $BeSO_4 \cdot 4H_2O$ to $BeSO_4 \cdot 2H_2O$ in contact with saturated solution was 88.3 ± 0.5°C. The compositions of saturated solutions in the above temperature ranges were obtained from the best fit of selected literature data. A correlation of relative vapor pressure lowering with relative saturation was developed which predicts the vapor pressures of undersaturated $BeSO_4$ solutions in the range 0–90°C.**

The vapor pressures of saturated, aqueous solutions of beryllium sulfate reported here form part of a thermodynamic study (*1*) of the system $BeSO_4$–$H_2O$. The disagreement existing among several authors (*3, 8, 12*) on the compositions of the stable hydrates and their transition temperatures in contact with saturated solution is now resolved. Vapor pressures and compositions of saturated solutions may be used as a basis for the prediction of the vapor pressures of undersaturated $BeSO_4$ solutions over wide ranges of temperature and composition.

### Experimental

A differential mercury manometer was constructed of 12-mm i.d. borosilicate glass tubing with side arms for sample and reference solutions. Water was distilled into both side arms, and an excess of $BeSO_4 \cdot 4H_2O$ was added to one side. The purity of the salt was previously reported (*1*). After several freeze-thaw degassing cycles, the entire manometer was evacuated and sealed under a vacuum of $1 \times 10^{-3}$ mm Hg. An oil bath controlled to ±0.01°C was used, and the temperature was measured to 0.01°C at both side arms with quartz thermometers.

The manometer levels were measured to 0.05 mm with a cathetometer, and the difference in levels was corrected to 0°C and $g = 9.80665$ m sec$^{-2}$. In this paper 1 mm Hg $\equiv$ 1 Torr = (101.325/760) kN m$^{-2}$. Occasional shaking ensured saturated solutions, and there was no significant difference between pressures obtained with heating and cooling. For measurements with a $BeSO_4 \cdot 2H_2O$ solid phase, a second run was carried out with a saturated sodium chloride solution as reference instead of water. The water vapor pressures over saturated aqueous NaCl were obtained from a least-squares fit of the data of several workers in the range 90–110°C (*11*), and the pressures over pure water were taken from standard tables (*13*).

### Results and Discussion

The measured water vapor pressures over saturated solutions in the range 25–89°C (Table I) are fitted by the least-squares relation:

$$\ln p_s = -15.3437 \ln T - 9927.89/T + 123.707 \qquad (1)$$

where $p_s$ is the pressure in mm Hg, and $T$ is the absolute temperature. The maximum deviation in $p_s$ is 0.95 mm Hg, and the standard deviation is 0.55 mm Hg. In the range 89–93°C the measured pressures are slightly lower than values predicted by Equation 1, the difference increasing to 3.5 mm Hg at 93°C.

On raising the temperature to 110°C, a period of 15 hr was required to reach a steady pressure, indicating a change to a lower solid hydrate. The measured water