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:

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

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 vapor pressures in the range 90–110°C (Table II) are best fitted by use of a coefficient for $\ln T$ of −15, suggested by Equation 1, giving the least-squares relation:

$$\ln p_s = -15 \ln T - 11016.1/T + 124.695 \qquad (2)$$

The maximum deviation in $p_s$ is 4 mm Hg, and the standard deviation is 2.9 mm Hg.

The two relations above intersect at 88.3 ± 0.5°C and a pressure of 351 mm Hg. The temperature is in excellent agreement with the values of Campbell et al. (*3*), 86.5–88.5°C from dilatometry and 89–90°C by extrapolation of isothermally invariant solution compositions to zero $H_2SO_4$ content. These workers showed the equilibrium solid phases to be $BeSO_4 \cdot 4H_2O$ at 85°C and $BeSO_4 \cdot 2H_2O$ at 95°C by X-ray analysis. Rohmer (*8*) claimed a transition to $BeSO_4 \cdot H_2O$ at 76°C, but the present vapor pressure vs. temperature curve shows no change of slope in this region and thus does not support such a claim.

More recently Vasil'ev et al. (*12*) reported 100°C and 300 mm Hg for the quadruple point where $BeSO_4 \cdot 4H_2O$, $BeSO_4 \cdot 2H_2O$, solution, and vapor are in equilibrium. The lack of agreement with the present work suggests that the thermal analysis method used by these workers did not allow equilibrium pressures to be measured.

Water vapor pressures over saturated solutions were also measured by Novoselova and Reshetnikova (*6*). Their values agree with Equation 1 within ±1 mm Hg in the range 20–50°C but then show a divergence increasing to 17.85 mm Hg at their upper limit of 70°C. Their pressure vs. temperature relation would never intersect the relation for $BeSO_4 \cdot 2H_2O$, Equation 2, as required for a transition, suggesting that their solutions may have been undersaturated in the 50–70°C range. The boiling point of the saturated solution at 760 mm Hg was reported by Campbell et al. (*3*) to be 108.2°C, in fair agreement with 107.8 ± 0.15°C predicted by Equation 2.

**Table I. Water Vapor Pressures over Saturated $BeSO_4$ Solutions and Water Reference**

| $t$, °C | $p_{ref}$ | $p_{obsd}$, mm Hg | $p_{calcd}$[a] | Approach[b] |
|---|---|---|---|---|
| 25 | 23.75 | 20.0 | 19.8 | HC |
| 35 | 42.18 | 35.1 | 35.2 | H |
| 45 | 71.88 | 59.15 | 59.3 | H |
| 55 | 118.04 | 95.1 | 95.5 | H |
| 60 | 149.38 | 118.95 | 119.25 | C |
| 65 | 187.54 | 147.4 | 147.4 | H |
| 70 | 233.7 | 181.0 | 180.5 | C |
| 75 | 289.1 | 219.95 | 219.05 | H |
| 80 | 355.1 | 264.2 | 263.55 | C |
| 85 | 433.6 | 315.4 | 314.5 | H |
| 87 | 468.7 | 336.8 | 336.85 | H |
| 89 | 506.2 | 359.3 | 360.25 | H |
| 90 | 525.85 | 370.7 | 372.4 | HC |
| 91 | 546.15 | 382.9 | 383.6 | H |
| 92 | 567.1 | 395.0 | 397.1 | H |
| 93 | 588.7 | 406.9 | 410.4 | H |

[a] Equation 1. [b] H, heating; C, cooling.

**Table II. Water Vapor Pressures over Saturated $BeSO_4$ Solutions and Saturated NaCl Reference**

| $t$, °C | $p_{ref}$ | $p_{obsd}$, mm Hg | $p_{calcd}$[a] | Approach[b] |
|---|---|---|---|---|
| 90 | 386.0 | 376.2 | 379.2 | C |
| 95 | 465.8 | 471.1 | 466.4 | C |
| 100 | 559.5 | 569.7 | 568.8 | C |
| 105 | 668.8 | 689.1 | 688.3 | C |
| 110 | 796.0 | 823.5 | 826.6 | H |

[a] Equation 2. [b] H, heating; C, cooling.

Further consideration of the data requires the composition of the saturated solutions. A critically selected set of data from the literature (Table III) is adequately fitted, in the range −10.5 to 88.4°C, by the least-squares relation:

$$m_s = 3.3879 + 1.7671 \times 10^{-2} t + 1.3082 \times 10^{-5} t^2 + 2.8728 \times 10^{-6} t^3 \qquad (3)$$

where $m_s$ is the molality of $BeSO_4$, and $t$ is the temperature in °C. The maximum and standard deviations in $m_s$ are 0.171 and 0.072 mole (kg $H_2O$)$^{-1}$, respectively. The data of Rohmer (*8*) for solution compositions over $BeSO_4 \cdot 2H_2O$, 7.179*m* at 101°C and 7.238*m* at 110°C, lie on a line meeting the curve for $BeSO_4 \cdot 4H_2O$, Equation 3, at 89°C. Thus, the transition temperature from solubility studies agrees with those found by other methods.

Isopiestic ratios of $BeSO_4$ to NaCl at 25°C for compositions extending into supersaturation were reported by Robinson (*7*). For the saturation composition of 3.883*m* given by Equation 3, these results give a pressure of 19.83 mm Hg, in good agreement with 19.8 mm Hg predicted by Equation 1. Similarly, vapor pressures of $BeSO_4$ solutions at 0° and 10°C measured by Fricke and Havestadt (*4*) may be extrapolated to saturation compositions of 3.388 and 3.569*m* to give pressures of 3.9 and 7.8 mm Hg, respectively, again in good agreement with 3.6 and 7.5 mm Hg predicted from Equation 1.

The vapor pressures and compositions of saturated solutions discussed above may be employed in the prediction of the vapor pressures of undersaturated solutions. Bencowitz and Hotchkiss (*2*) reported that the lowering of vapor pressure, relative to that of a saturated solution, is a temperature-independent function of the relative saturation:

$$(p_o - p)/(p_o - p_s) = f(m/m_s) \qquad (4)$$

**Table III. Composition of Saturated $BeSO_4$ Solutions**

| | Mole $BeSO_4$ (kg $H_2O$)$^{-1}$ | |
|---|---|---|
| $t$, °C | $m_s$, obsd[a] | $m_s$, calcd[b] |
| −10.5 | 3.206 (*8*) | 3.201 |
| 0.6 | 3.379 (*8*) | 3.399 |
| 20.0 | 3.700 (*8*) | 3.770 |
| 25.0 | 3.907 (*6*), 3.831 (*9*)<br>4.046 (*10*), 3.930 (*3*) | 3.883 |
| 30.0 | 4.077 (*6*), 4.030 (*5*)<br>4.040 (*9*) | 4.007 |
| 32.8 | 3.926 (*8*) | 4.083 |
| 36.0 | 4.079 (*8*) | 4.175 |
| 40.0 | 4.298 (*5*), 4.356 (*9*) | 4.300 |
| 42.0 | 4.275 (*8*) | 4.366 |
| 50.0 | 4.734 (*10*), 4.675 (*3*)<br>4.605 (*8*) | 4.663 |
| 60.0 | 5.103 (*9*), 5.127 (*10*) | 5.116 |
| 61.0 | 5.170 (*8*) | 5.167 |
| 68.0 | 5.590 (*9*) | 5.553 |
| 68.8 | 5.734 (*8*) | 5.601 |
| 75.0 | 5.828 (*3*), 6.034 (*8*) | 5.999 |
| 80.0 | 6.345 (*8*) | 6.356 |
| 85.0 | 6.705 (*3*), 6.780 (*8*) | 6.749 |
| 88.4 | 7.064 (*8*) | 7.037 |
| 90.0 | 7.180 (*8*) | 7.179 |

[a] Reference numbers in parentheses. [b] Equation 3.

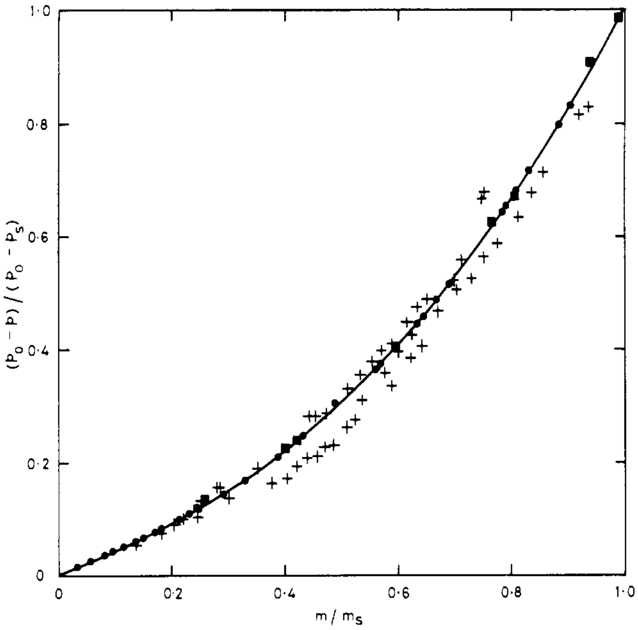

**Figure 1.** Relative vapor pressure lowering vs. relative saturation for aqueous $BeSO_4$
● 25°C (*7*)
■ 0.10°C (*4*)
+ 19.87–100°C (*11*)

where $p_o$, $p$, and $p_s$ are the vapor pressures of water, solution, and saturated solution, respectively, at a given temperature; $m$ and $m_s$ are the molalities of solution and saturated solution, respectively, at that temperature. This relation applied to a variety of salts in water over the range 20–90°C (*2*). The application to $BeSO_4$ may be tested with $p_s$ and $m_s$ values from Equations 1 and 3 with literature data for $p$ and $m$ at various temperatures.

The carefully measured data of Robinson (*7*) at 25°C lie on a smooth curve (Figure 1), and the data of Fricke and Havestadt (*4*) at 0° and 10°C agree with this curve within their accuracy of measurement. A large set of early data by Tamman [reported by Timmermans (*11*)] in the range 19.87–100°C has considerable scatter and doubtful accuracy but nevertheless agrees well with the curve. Accordingly, the curve shown, together with $p_s$ and $m_s$ values from Equations 1 and 3, may be used to predict solution vapor pressures for molalities up to saturation and temperatures in the range 0–90°C.

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# Heat of Combustion of *N,N'*-bis(*m*-methoxyphenyl)terephthalamide and *N,N'*-bis(*p*-methoxyphenyl)terephthalamide

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**The heats of combustion of crystalline *N,N'*-bis(*m*-methoxyphenyl)terephthalamide and *N,N'*-bis(*p*-methoxyphenyl)terephthalamide in the standard state at 25°C, $\Delta H°_{c(c)}$ are −2621.21 ± 0.76 and −2621.01 ± 0.71 kcal $mol^{-1}$, respectively. Enthalpies of formation in the condensed and the gaseous state are derived.**

In continuation of a study of the thermodynamic properties of terephthalamides and related compounds, we have measured the heat of combustion of *N,N'*-bis(*m*-methoxyphenyl)terephthalamide and *N,N'*-bis(*p*-methoxyphenyl)terephthalamide. The heats of combustion of these compounds have not been previously reported in the literature.

## Experimental

***Apparatus and procedures.*** The apparatus and experimental procedures were described previously (*5*). The temperature rise of about 2.7°C was measured by quartz thermometry. The internal volume of the bomb was 0.344 liter. The sample pellets were weighed to an accuracy of 0.01 mg, and corrections for air buoyancy were applied.

Ignition was accomplished by fusing a 10-cm length of 44-swg platinum wire wrapped around a small piece (~4 mg) of Whatman No. 1 filter paper. The heat of combustion of the filter paper was taken as 4118 ± 10 cal $g^{-1}$ (*11*). The electrical ignition energy was measured with a current integrator similar to that used by Pilcher and Sutton (*8*). The extent of combustion was based on the mass of sample. All calculations, including conversion of time and temperature measurements to initial and final temperatures, correction for heat exchange between calorimeter and jacket, and reduction to the standard state, were carried out on a digital computer (*13*). The computer program followed the procedure of Hubbard et al. (*6*).

***Materials.*** *N,N'*-bis(*m*-methoxyphenyl)terephthalamide was synthesized by reacting *m*-anisidine with dithioterephthalic acid according to Caswell et al. (*2*). *N,N'*-bis(*p*-methoxyphenyl)terephthalamide was synthesized in a like manner by reacting *p*-anisidine and dithioterephthalic acid. The crystalline solids were purified by washing with 5% sodium hydroxide, rinsed with distilled water until the

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