

## VAPORS AND THE GAS LAWS

CREIG S. HOYT, GROVE CITY COLLEGE, GROVE CITY, PENNSYLVANIA

*The vapors of liquids at or near the boiling point occupy a smaller volume than is calculated by the simple gas laws. A simple correction,  $\frac{P_c - 1.32}{P_c}$ , is applied to the gas constant to compensate for this deviation. The correction, which is derived from Berthelot's equation, has been evaluated for several of the common liquid compounds.*

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The physical chemist finds numerous occasions when he encounters pressure-volume-temperature relations of the vapors of compounds which are normally liquid. In vapor density methods for the determination of molecular weights, in the Clausius-Clapeyron equation for vapor pressures, in the thermodynamic computation of the ebullioscopic constants; in these and many other instances, it is necessary either to assume that the vapors of liquids follow the gas laws with sufficient exactness or to apply a correction for the deviation from the simple laws.

Of the various equations of state proposed for this purpose the simplest and most widely used is that of van der Waals, which corrects both for the attractive force between the molecules and for a lack of compressibility at high pressures. D. Berthelot (1) has modified the equation to express the arbitrary constants  $a$  and  $b$  in terms of the critical conditions and with the volume at the limit of compressibility equal to a quarter rather than a third of the critical volume as would be indicated by the original equation. This has been found to apply with great exactness to a wide variety of substances over a considerable range of pressures. In spite of its obvious advantages, it appears somewhat formidable to one who has never attempted it.

$$PV = RT \left[ 1 + \frac{9}{128} P/P_c \frac{T_c}{T} \left\{ 1 - 6 \frac{T_c^2}{T^2} \right\} \right]$$

Nernst (2) has utilized a simpler empirical equation for the correction of vapor pressure data in the computation of the latent heat of vaporization. His equation is

$$PV = RT [1 - P/P_c]$$

It may be demonstrated that this form is not a correct one, but its use is much more accurate than the common practice of making no correction at all.

Inasmuch as the necessity for a correction arises most frequently in the case of a saturated vapor at the temperature of normal ebullition or near this temperature, a special form of the Nernst equation applicable to this particular case is valuable. Such a relation may be derived from the Berthelot equation.

Guldberg and Guye (3) have shown that the boiling point of a liquid on the absolute scale is approximately two-thirds of the critical temperature on the same scale. Assuming this ratio to be correct, we may substitute 1.5 for  $T_c/T$  in all cases and regardless of the nature of the substance. With this substitution the Berthelot equation becomes

$$PV = RT [1 - 1.32 P/P_c]$$

or, when the critical pressure is expressed in atmospheres

$$PV = RT \left[ \frac{P_c - 1.32}{P_c} \right]$$

The form of the equation indicates immediately the sign and the approximate magnitude of the correction. Where the critical pressure is very great, the correction is small as in the case of water vapor. On the other hand, when the critical pressure is small, the correction is rather important. To ignore the necessity for correction involves an error of 3.4% with benzene, 1.5% with alcohol, and 4% with ether. All this is readily shown by the equation proposed with none but the simplest computation.

It is apparent that as the temperature rises above the normal boiling point, the constant correction term will approach that of the Nernst equation, but at temperatures below the boiling point the constant is greater than that shown. Above or below the boiling temperature, the universality of the temperature relationship disappears and the constant of the equation becomes different for each substance.

Table I shows a comparison of the corrections to be applied; (1) calculated from the Berthelot equation, (2) from the Nernst equation, (3) the proposed equation, and (4) from the density of the saturated vapor at the temperature of normal ebullition as taken from the Chemical Rubber Co., Handbook of Chemistry and Physics. It is apparent that certain of the density data are erroneous and that the corrections, calculated from the proposed equation, are at least as accurate as the quality of the available data would require.

TABLE I  
Correction to Be Applied to Volumes of Saturated Vapors at Normal Boiling Point

	<i>Proposed Equation</i>	<i>Berthelot Equation</i>	<i>Nernst Equation</i>	<i>Observed</i>
Benzene	0.9725	0.9658	0.9791	0.9791
Alcohol	0.9790	0.9844	0.9840	0.9739
Water	0.9932	0.9900	0.9949	0.9872
Chloroform	0.9759	0.9693	0.9818	0.9825
Ether	0.9631	0.9607	0.9721	0.9435
Methanol	0.9832	0.9814	0.9872	0.9551

As an example of the value of the correction, we may cite the calculation of the latent heat of vaporization of benzene from the vapor pressures.

Over the range from 70 to 80°C. Nernst (4) calculated the latent heat by the formula

$$\lambda = 1.985 \times 2.303 \frac{T_1 T_2}{T_2 - T_1} \log \frac{P_2}{P_1}$$

to be 7620 calories per mol, while the observed value is 7426 calories.

Applying the correction term,  $\frac{P_c - 1.32}{P_c}$ , which in this case is equal to 0.9725, the calculated value is 7417 calories, in excellent agreement with the observed heat of vaporization.

#### Literature Cited

- (1) D. BERTHELOT, "Sur les thermomètres à gaz," Gauthier-Villars, Paris, 1903.
  - (2) NERNST, "Theoretical Chemistry," fifth edition, Macmillan & Company, Ltd., London, 1923, p. 317.
  - (3) GULDBERG, *Z. physik. Chem.*, **5**, 374 (1890).
  - (4) NERNST, "Theoretical Chemistry," fifth edition, Macmillan & Company, Ltd., London, 1923, p. 67.
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