mination is therefore purposely omitted. How·ever, the mobilities were used for identification of the components.

It will be noted that the albumin–globulin ratio is distinctly lower in the hypophysectomized rat serum in comparison with normal serum. The percentage lowering of this ratio is about 53.0. This is somewhat higher than that found by Levin,[5] who obtained a percentage lowering of .46.0.

Addendum.—While this note was in the hands of the Editors, an article by Moore, *et al.*,[12] appeared in which they found that the normal rat serum lacks the α-globulin. It may be noted in Fig. 1 that the appearance of this component is evident. It is possible that the sera they used are too dilute to escape the detection of a small concentration of the α-globulin component.

(12) D. H. Moore, L. Levin and J. H. Leathem, *J. Biol. Chem.*, **153**, 349 (1944).

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The Determination of Water in Formic Acid

BY J. MITCHELL, JR., AND WALTER HAWKINS

In a previous publication from this Laboratory[1] the Karl Fischer reagent was not recommended for the determination of water in the presence of formic acid, presumably because of dehydration of the acid. Later studies on this system have indicated that under normal conditions this interference is not appreciable, amounting to only a fraction of a per cent. in high concentrations of formic acid.

Experimental

Aqueous solutions of the acid were prepared by adding various amounts of water to Eastman Kodak Company formic acid.. Weighed samples were analyzed for water by direct titration with Karl Fischer reagent and for free acid by titration with standard alkali. Results are summarized in the following table.

THE DETERMINATION OF WATER IN FORMIC ACID

Water, wt. %		Acid, wt. %		Total, wt. %
89.85	± 0.05	10.22	± 0.01	100.07
70.30	0.10	29.76	0.02	100.06
26.1	0.1	74.0	0.2	100.1
14.80	0.00	85.20	0.00	100.00
1.55	0.05	98.80	0.02	100.35

(1) Smith, Bryant and Mitchell, THIS JOURNAL, **61**, 2407 (1939).

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The van der Waals Constant "a" from C_p/C_v Measurements

BY R. E. RUNDLE

By an improved resonance method Clark and Katz[1] have succeeded in obtaining accurate meas-

(1) Clark and Katz, *Can. J. Research*, **18A**, 23 (1940); **21A**, 1 (1943).

urements of γ, (C_p/C_v), as a function of pressure for a number of gases. They find experimentally that for simple gases the variation of γ with pressure is linear, and they show that this is the expected behavior of a gas whose equation of state is $PV = RT + BP$. It is also interesting to note that a linear dependence of γ on pressure is to be expected for a van der Waals gas at moderate pressures, and that from the slope of the curve, γ vs. P, the van der Waals constant a can be determined.

For a substance whose properties are a function of P and T only[2]

$$C_p - C_v = T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V \tag{1}$$

For a mole of van der Waals gas

$$(P + a/V^2)(V - b) = RT \tag{2}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - b} \tag{3}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P - a/V^2 + 2ab/V^3} \tag{4}$$

Substituting (2), (3) and (4) in (1), and ignoring $2ab/V^3$ with respect to a/V^2

$$C_p - C_v = R \frac{P + a/V^2}{P - a/V^2} \tag{5}$$

In the term a/V^2 it suffices to use the molal volume from the perfect gas equation. Then

$$C_p - C_v = R \frac{(RT)^2 + aP}{(RT)^2 - aP}, \text{ or} \tag{6}$$

$$\gamma = \left(\frac{R}{C_v} + 1\right) + \frac{R}{C_v} \frac{2aP}{(RT)^2} + \cdots \tag{7}$$

where the coefficients of higher powers of P are small, so that the extra terms may be ignored at moderate pressures. It is to be noted that C_v is independent of pressure for a van der Waals gas, so that $C_v = R/(\gamma_0 - 1)$, and the dependence of γ on pressure is linear.

If terms in higher powers of P are necessary, the term in b cannot be ignored. In this case

$$\gamma = 1 + R/C_v \left[1 + \frac{2aP}{(RT)^2} + \frac{2a}{(RT)^3} (a/RT - b)P^2 + \cdots \right] \tag{8}$$

For certain gases, Clark and Katz find that γ at constant T must be expressed in terms of an equation of the form

$$\gamma = \gamma_0 + C_1 P + C_2 P^2 + \cdots$$

but the correlation with equation (8) is not good. Apparently the approximation of a real gas by the van der Waals equation is not sufficient to make the coefficient of P^2 in (8) significant. It appears, however, that the coefficient of P can be used to calculate a, just as in equation (7).

Equation (7) has been applied to data of Clark and Katz[1,3] to obtain a for a number of gases. In the table these values of a are compared with

(2) Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, N. Y., 1923, p. 136.

(3) Clark and Katz, *Can. J. Research*, **19A**, 111 (1941).