mination is therefore purposely omitted. However, 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.

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[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

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[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 measurements 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

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

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

$$\gamma = \gamma_0 + C_1P + C_2P^2 + \ldots$$

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

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

[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).

those calculated from critical data.[4] The agreement is good for the simpler gases for which equation (7) is valid. For the gases CO_2, N_2O and SO_2, not well represented by the van der Waals equation, the values of a from the critical constants are not satisfactory at temperatures and pressures far from the critical conditions, and hence cannot be expected to agree well with the values of a calculated from other data. It is interesting that PVT data[5] for carbon dioxide at pressures and temperatures more nearly comparable with those of Clark and Katz yield values of a in the neighborhood of 4 to 6, while similar calculations from sulfur dioxide data[6] give values of a as high as 10–15. The values of a from (7) are probably as reliable as any for gases which show large deviations from van der Waals behavior, and like other values of a for such gases, they are useful only over limited ranges of pressure and temperature.

Values of γ at zero pressure can be obtained from molecular and spectral data, and equation (7) should provide a simple, approximate correction to moderate pressures. But it is evident from the table that if values of a are taken from critical data, equation (7) is accurate only for gases which are well represented by the van der Waals equation.

TABLE I

VALUES OF a IN ATM. $L.^2/MOLES^2$

Gas	a (from eq. 7)	a (critical data)
A	1.57	1.345
H_2	0.234	0.244
N_2	1.63	1.390
CO_2	5.02	3.59
N_2O	6.80	3.78
SO_2	19.2	6.71

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(4) Lange, "Handbook of Chemistry," fourth ed., Handbook Publishers, Inc., Sandusky, Ohio, 1941, pp. 1307–1309.

(5) Cooper and Maass, *Can. J. Research*, **4**, 283 (1931).

(6) Cooper and Maass, *ibid.*, **4**, 495 (1931).

DEPARTMENT OF CHEMISTRY
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[CONTRIBUTION FROM ALLERGEN INVESTIGATIONS, BUREAU OF AGRICULTURAL AND INDUSTRIAL CHEMISTRY, AGRICULTURAL RESEARCH ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE, AND THE ALLERGY CLINIC OF PROVIDENCE HOSPITAL, WASHINGTON, D. C.]

The Chemistry of Allergens. X. Comparison of Chemical and Immunological Properties of CB-1A Preparations from Domestic Castor Beans and Brazilian Castor Bean Pomace[1,2]

BY JOSEPH R. SPIES, E. J. COULSON AND HENRY STEVENS

The allergenic fraction, CB-1A, was originally isolated from a domestic variety of castor beans.[3] Before application of the isolation procedure, it was necessary to shell, grind and defat the seeds. In investigations involving castor beans it is necessary to curtail handling as much as possible because of the hazard associated with the primary toxalbumin, ricin[4,5] and because of the possibility of acquiring sensitivity to the castor bean allergen by continued exposure to dust.[6] In an effort to simplify the procedure and to lessen the hazards involved in isolating a large quantity of CB-1A, an examination of Brazilian castor bean pomace was undertaken. The pomace was used directly without ether extraction, and a preliminary heat treatment was employed to detoxify the ricin.

A yield of 0.45% CB-1A was obtained from the pomace as compared with 1.8% previously obtained from one lot of shelled, defatted, domestic castor beans.[3,7] Results in Table I show the close similarity in chemical composition of the CB-1A obtained from the two sources.

TABLE I

COMPARISON OF CHEMICAL COMPOSITION OF CB-1A FROM SHELLED, DOMESTIC CASTOR BEANS AND FROM BRAZILIAN CASTOR BEAN POMACE

	Composition in % of CB-1A from	
Determination[a]	Domestic castor beans[b]	Brazilian castor bean pomace
Nitrogen	18.4	18.2
Nitrogen pptd. by 5% trichloroacetic acid at 20 ± 0.1°	30.7[c]	39.4
Sulfur	2.33	2.36
Carbohydrate	3.12	3.10
Arginine	26.6	26.6
Cystine	5.0	4.1
Tyrosine	1.1	1.1
Tryptophan	0.0	0.0

[a] Analyses are expressed on an ash-water-free percentage basis. The authors are indebted to Dorris C. Chambers for the microanalytical determinations. Amino acid determinations are expressed on the basis of per cent. of the total nitrogen in the form of the given amino acid. Tyrosine was determined by Lugg's procedure, *Biochem. J.*, **31**, 1422 (1937); **32**, 775 (1938). Other methods were the same as those used in Paper VIII.[3] [b] Isolation of this sample of CB-1A is described in Paper VIII.[3] [c] It was reported in Paper VIII[3] that 22.5% of the nitrogen of CB-1A from domestic castor beans was precipitated by 5% trichloroacetic acid. This value was in error owing to inadvertent use of a lower concentration of trichloroacetic acid.

The samples of CB-1A from both sources were immunologically equivalent. Both samples were equally potent in producing contractions in excised uterine strips of sensitized guinea pigs by the Schultz–Dale technique, using the multiple in-

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(2) For Article IX of this series see Spies, Coulson, Chambers, Bernton and Stevens, THIS JOURNAL, **66**, 748 (1944).

(3) Spies and Coulson, *ibid.*, **65**, 1720 (1943).

(4) Stillmark, "Arbeiten des Pharmakologischen Instituts Zu Dorpat," 1889; *Chem. Zentr.*, [2] **60**, 978 (1889).

(5) Osborne, Mendel and Harris, *Am. J. Physiol.*, **14**, 259 (1905).

(6) Figley and Elrod, *J. Am. Med. Assoc.*, **90**, 79 (1928); Vaughn, *J. Allergy*, **1**, 474 (1930); Coca, Walzer and Thommen, "Asthma and Hay Fever in Theory and Practice," Charles C. Thomas, Baltimore, 1931, pp. 42, 175–176, 405.

(7) The lower yield of CB-1A from the pomace is attributed to natural differences which occur in the content of plant constituents from different sources or species and is not attributed to the slightly modified isolation procedure used.