treating 2 kg. of fresh wheat germ with 5 liters of water and 50 g. of sulfosalicylic acid followed by filtering, centrifuging and precipitation of the supernatant liquid with neutral lead acetate. The lead precipitate was ground with 0.5 N sulfuric acid, centrifuged and filtered and the copper, mercury and silver salts precipitated successively in the usual way. The final silver salt precipitate was treated with hydrogen sulfide and filtered. Absolute ethanol was added to the filtrate and the solution evaporated rapidly to dryness in a vacuum desiccator over phosphorus pentoxide. It is very difficult to remove the last traces of ash from glutathione prepared from wheat germ and most of our preparations have contained about 1% ash. The best means of purification is through successive silver salt precipitations.

The analysis of the purified product was as follows: C, 38.86, 38.78; H, 5.49, 5.47; N(corr. 24°, 761 mm.), 13.41, 13.43. The theoretical results for $C_{10}H_{17}N_3SO_6$ are C, 39.06; H, 5.57; N, 13.68. The melting point of our preparation was 189–190° (evolution of carbon dioxide) with previous softening at 147°. Harington and Mead[2] report a melting point of 190° for pure synthetic glutathione.

The presence of glutathione in wheat germ is responsible for the deleterious action of the germ on the baking quality of flour.

(2) Harington and Mead, *Biochem. J.*, **29**, 1602 (1935).

RUSSELL MILLER MILLING CO.
MINNEAPOLIS, MINN. RECEIVED NOVEMBER 8, 1937

A Simplified General Equation of State

BY GEORGE WOOLSEY

A critical study of the general equation of state[1] has resulted in a slightly changed form and a simplification which makes the determination of its constants considerably less difficult. For the particular value of the critical coefficient, $n_0 = 3.25$, to which all data may be converted by means of the stretch formula, the volume coefficient, B, may be set equal to zero. The new form then becomes

$$\left(P + \frac{A}{T^{1/2}V^2 + CT^yV + DT^z}\right) V = 3.25\ T + KP + q \log\left(\frac{P}{T} + 1\right)$$

Making the equation a perfect cubic at the critical point gives the relationships

$$A = \frac{(C+2)^3}{C+3} \qquad D = \frac{1}{C+3}$$

$$K = C + 3 - n - 0.30103q = C - 0.25 - 0.30103q$$

The relationship at the Boyle temperature becomes

$$q' = \frac{A}{nT_B{}^{0.5}} - KT_B \text{ where } q' = 0.434294q$$

Evaluating the constants by fitting the equation at $P = 20$ and 10 at $T = 1$ makes them

$$C = 0.83429,\ D = 0.26080,\ A = 5.93811$$
$$K = 0.28694,\ q = 0.98777$$

and $T_B = 2.518$. The equation, with these constants, fits well along the entire critical isotherm.

The values of y and z can be determined by use of the relationships, $0.5 + Cy + Dz = 0$[1] and

$$\left[\left(\frac{\partial^2 P}{\partial T^2}\right)_V\right]_{\text{Cr}} = 0$$ [2]

From these relationships

$$0 = \frac{C+3}{C+2}\left\{\frac{C}{D}(C+D)\,y^2 + \frac{C}{D}\,y + 0.25C + 1\right\} - \frac{q'}{4}\left[\left(\frac{\partial P}{\partial T}\right)_V\right]^2_{\text{Cr}} - \frac{q'}{2}\left[\left(\frac{\partial P}{\partial T}\right)_V\right]_{\text{Cr}} + \frac{3}{4}\,q'$$

where

$$\left[\left(\frac{\partial P}{\partial T}\right)_V\right]_{\text{Cr}} = \frac{n - \frac{q'}{2}}{1 - K - \frac{q'}{2}}$$

Solving these equations, $y = 0.49736$, and $z = -3.50821$. The equation with these constants fits all regions up to $P = 86$ fairly well except for the liquid phase in equilibrium with the vapor. It can be made to fit in this last-named region by slight changes in the values of y and z, dropping only the condition that the above second derivative equal zero. Incidentally, it might be mentioned that this equation shows the existence of a unique point[3] at $P = 11$ and $T = 2$ to 3.5 as found experimentally.

Above $P = 86$ the extreme pressures seem to decrease the effective volumes of the molecules so that a new term needs to be introduced into the equation. Writing it

$$\left(P + \frac{A}{T^{1/2}V^2 + CT^yV + DT^z}\right)V = nT + \left(K - \alpha\frac{P^w}{T^x}\right)P + q\log\left(\frac{P}{T} + 1\right)$$

where α, w and x are new constants, it is possible to fit it to the high pressure nitrogen data up to $P = 433$, the limit of the experimental determinations. Work with the equation in this form indicates at present that best results are obtained

---

(1) Woolsey, THIS JOURNAL, **58**, 984–987, 2229–2231 (1936).

(2) R. Plank, *Forsch. Gebiete Ingenieur.*, Band 7, 161–173 (1936).

(3) Bartlett, *et al.*, THIS JOURNAL, **52**, 1363–1381 (1930).

by using the experimental value of n and letting $w = {}^1/_3$. In changing to this form the expressions for A, D, T_B and $0.5 + Cy + Dz = 0$ do not change but the other relations become

$$K - \alpha = C + 3 - n - 0.30103q$$

$$\left[\left(\frac{\partial P}{\partial T}\right)_V\right]_{\mathrm{Cr}} = \frac{n + \alpha x - \frac{q'}{2}}{1 - K + (w + 1)\alpha - \frac{q'}{2}}$$

$$0 = \frac{C + 3}{C + 2}\left\{\frac{C}{D}(C + D)y^2 + \frac{C}{D}y + 0.25C + 1\right\} - \left\{\frac{q'}{4} + w\,(w + 1)\alpha\right\}\left[\left(\frac{\partial P}{\partial T}\right)_V\right]^2_{\mathrm{Cr}} - \left\{\frac{q'}{2} - 2x\,(w + 1)\alpha\right\}\left[\left(\frac{\partial P}{\partial T}\right)_V\right]_{\mathrm{Cr}} - x\,(x + 1)\alpha + \frac{3}{4}q'$$

The constants, as determined for nitrogen, are $n = 3.427$, $C = 1.007$, $D = 0.24956$, $A = 6.78549$, $q = 0.72330$, $K = 0.38022$, $\alpha = 0.01796$, $x = 0.16798$, $y = 0.37965$, $z = -3.53541$, $w = {}^1/_3$, $T_B = 2.48$.

By converting values found by this equation to $n = 3.424$, the value for argon, by means of the stretch formula the changes in volume correspond closely with the experimentally determined volume changes for argon[4] from 2000–15,000 kg./sq. cm. at 55° and the volume at 3000 kg./sq. cm. and 55° is found to be 0.765 cc./g.

---

(4) P. W. Bridgman, "The Physics of High Pressure," The Macmillan, Co., New York, N. Y., 1931.

VALENCIA HIGH SCHOOL
PLACENTIA, CALIF.

RECEIVED SEPTEMBER 20, 1937

COMMUNICATIONS TO THE EDITOR

THE EFFECT OF HYDROXYL GROUPS ON THE APPARENT DIENE VALUES OF VEGETABLE OILS AND FATS

Sir:

In a letter to the editor of *Chemistry and Industry*, **56**, 937 (1937), entitled, "Maleic Anhydride Value or Diene Value," R. J. Bruce and P. G. Denley called attention to certain anomalous results which they obtained on determining the M. A. V. of oxidized linseed, perilla, and soybean oils. They state "It occurred to us that the M. A. V. might not be solely indicative of conjugated double bonds, but that it might include any maleic anhydride that entered into combination with hydroxyl groups already in the oil or formed during oxidation."

In order to test the validity of this assumption they determined the M. A. V. of dihydroxystearic acid, blown oleic acid, commercial castor oil, and blown linseed, perilla, and soybean oils by the Ellis and Jones method using a one-hour period of reflux. Maleic anhydride values, ranging from 5.2 in the case of blown oleic acid to 31.4 for dihydroxystearic acid, were observed.

This Laboratory has been engaged for some months on a study of the applicability of the Ellis and Jones, and the Kaufmann, Baltes, and Büter, diene methods, as a means of following changes in the polyethenoid linkages of soybean oil under various conditions of heat bodying. As in the case of Bruce and Denley, it was noted that the presence of hydroxyl groups led to anomalous diene values. Consequently, the M. A. V. and diene value of a number of purified hydroxylated compounds were determined before and after blocking the hydroxyl group by acetylation. The compounds examined included methyl 12-hydroxystearate, glyceryl monoricinoleate, methyl ricinoleate, α-monopalmitin, α,α'-distearin, ethylene glycol, acetone-glycerol, and glycerol. It was observed that in all but one case (α,α'-distearin) significant M. A. V. and diene values were observed with the hydroxylated compounds; whereas, following acetylation, the magnitude of these values dropped in all cases to practically zero.

In a similar manner were examined a variety of oils, including, besides variously treated soybean oils, also linseed, castor, perilla, oiticica, and tung. Castor oil exhibited the characteristic behavior of hydroxylated compounds, giving an appreciable M. A. V. and diene value which fell to nearly zero after acetylation. Tung oil also exhibited a small decrease in M. A. V. and diene value after acetylation. However, the M. A. V. and diene values of linseed and soybean oils, which were initially low, rose appreciably after acetylation. In the case of these two oils the increase in the diene value (800–1000 per cent.) was accompanied by an increase in