TABLE I

PERCENTAGE DECREASES IN VALUES FOR TRUE PROTEIN, SOLUBILITY AND DIGESTIBILITY OF PROTEIN, AFTER STORAGE OF SOYBEAN MEAL UNDER DIFFERENT CONDITIONS FOR ONE, THREE, AND SIX MONTHS

Storage conditions		True Protein. %			Extractability. %			Digestibility. %		
		1 mo.	3 mos.	6 mos.	1 mo.	3 mos.	6 mos.	1 mo.	3 mos.	6 mos.
STORED IN JARS										
High-fat meal	30°F.	0.31	2.88	4.35	1.18	3.08	4.53	0.92	5.61	7.26
High-fat meal	76°F.	2.15	4.83	7.16	2.92	5.91	8.71	4.53	9.49	12.05
Low-fat meal	30°F.	3.01	4.21	5.44	1.51	5.04	7.53	3.80	10.41	12.97
Low-fat meal	76°F.	3.95	6.36	8.71	3.82	8.47	10.72	5.57	15.30	17.25
STORED IN BAGS[a]										
High-fat meal	30°F.	..	..	5.85	..	..	8.92	..	...	10.43
High-fat meal	76°F.	..	..	8.75	..	..	13.11	..	...	14.48
Low-fat meal	30°F.	..	..	6.76	..	..	8.94	..	...	15.13
Low-fat meal	76°F.	..	..	9.97	..	..	12.39	..	...	18.94

[a] Analyses of meals stored in bags were made only after six months' storage.

interest is the consistently greater changes that occurred in the low-fat samples than in the high-fat samples. The total nitrogen and free ammonia content of all the samples remained constant throughout the storage periods. The high-fat samples showed a slight increase in free fatty acids, particularly in the samples stored at 76°.

Storage of soybean meal apparently results in partial denaturation of the proteins as indicated by their decreased solubility in salt solution. A proteolysis is also indicated by the drop in true protein values. The nature of the marked decrease in digestibility *in vitro* is being studied.

The chemical studies outlined above are being supplemented by feeding experiments to determine the effects of storage on the biological value of the proteins. Storage studies on the samples will be continued for two years or more. Final results and details of the work will be published later. Similar studies on the proteins of other seeds of importance as foodstuffs will be made both on the meals and on the whole grains.

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The Standard Electromotive Force of the Lead Electrode

BY JAMES J. LINGANE

There is considerable uncertainty in the literature regarding the standard e. m. f. of the lead electrode. The value 0.122 v., given in the "International Critical Tables,"[1] was calculated by Lewis and Randall,[2] from Gerke's measurements[3] of the cell $Pb/PbCl_2$, $AgCl(s)/Ag$, and an activity coefficient of saturated lead chloride computed from the data of Brönsted.[4]

Carmody[5] later studied this cell more carefully, extending the measurements to very small concentrations of lead chloride, and he obtained the value 0.1263 v. for E^0_{Pb} at 25°. Using the accurate activity coefficients of lead chloride obtained from his measurements, Carmody recalculated E^0_{Pb} from Gerke's data and obtained the value 0.1264 v., which agrees very well with his own value.

However, Randall and Cann,[6] in an apparently equally careful study, later obtained the value 0.1203 v. for E^0_{Pb}, from their measurements of the cell $Pb/Pb(NO_3)_2/KNO_3/KCl$, $AgCl(s)/Ag$ with *flowing* liquid junctions. Carmody recently[7] has attributed this lower value of Randall and Cann to the fact that they flowed the cell solutions *directly* over the silver–silver chloride electrodes. He has shown[8] that flowing the electrolyte directly over silver–silver chloride electrodes causes their potential to become about 6 mv. positive to the same electrodes in equilibrium with the cell solution. When this correction of 6 mv. is applied to the data of Randall and Cann, the corrected value becomes 0.1263 v., in exact agreement with Carmody's value.

Since this correction is somewhat uncertain, and may depend on the method of preparing the silver–silver chloride electrodes, it is very desirable to obtain further evidence before it is accepted.

The standard e. m. f. of the lead electrode can

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(1) "International Critical Tables," Vol. VI. 1929. p. 332.

(2) G. N. Lewis and M. Randall. "Thermodynamics." McGraw-Hill Book Co., Inc., New York. N. Y., 1923. p. 424.

(3) R. H. Gerke. THIS JOURNAL. **44**, 1684 (1922).

(4) J. N. Brönsted. *Z. physik. Chem.*, **56**, 645 (1906).

(5) W. R. Carmody. THIS JOURNAL, **51**, 2905 (1929).

(6) M. Randall and J. Y. Cann, *ibid.*, **52**, 589 (1930).

(7) W. R. Carmody. *ibid.*, **54**, 210 (1932).

(8) W. R. Carmody. *ibid.*, **54**, 188 (1932).

be evaluated from the standard e. m. f. of the lead–lead sulfate electrode and the activity product, K, of lead sulfate by means of the relation

$$E^0_{\mathrm{Pb}} = E^0_{\mathrm{PbSO_4}} + (RT/2F)\ln K \qquad (1)$$

in which E^0_{Pb} is the standard e. m. f. of the lead electrode, $\mathrm{Pb/Pb^{++}}$ ($a = 1$), and $E^0_{\mathrm{PbSO_4}}$ is the standard e. m. f. of the lead–lead sulfate electrode, $\mathrm{Pb/PbSO_4(s), SO_4^{=}}$ ($a = 1$).

According to Harned and Hamer[9] the standard potential of the *two-phase lead amalgam*–lead sulfate electrode is 0.3495 v. at 25°. This is in agreement with the value 0.3505 v. given by Shrawder, Cowperthwaite, and La Mer.[10] We will use the average value 0.3500 ± 0.0005 v. Since the potential of two-phase lead amalgam against solid lead is 0.0058 v.,[3,5,6] the standard e. m. f. of the *solid lead*–lead sulfate electrode becomes 0.3558 v.

Kolthoff and von Fischer[11] recently have completed a study in this Laboratory of the *solubility* of lead sulfate by the conductance method and by direct analysis of the saturated solutions. From their data the solubility of lead sulfate at 25° is $1.48\ (\pm 0.02) \times 10^{-4}$ molar. This is in good agreement with the value 1.47×10^{-4} molar given by Crockford and Brawley,[12] and the value 1.48×10^{-4} molar taken from the data of Kolthoff and Rosenblum.[13]

The activity coefficient of lead sulfate in its saturated solution, computed from the Debye–Hückel limiting law, is 0.893. Using the extended Debye–Huckel equation, with the plausible value of 4 Å. for the ion-size parameter, the calculated activity coefficient is 0.897. From this value, and the value $1.48\ (\pm 0.02) \times 10^{-4}$ molar for the solubility of lead sulfate, the activity product of lead sulfate at 25° is $1.76\ (\pm 0.04) \times 10^{-8}$.

By substituting these data into eq. (1), we find for the standard e. m. f. of the *solid* lead electrode

$$E^0_{\mathrm{Pb}} = 0.3558 + \frac{0.05915}{2}\log(1.76 \times 10^{-8}) = 0.1264 \text{ v.} \qquad (2)$$

This value, computed from independent data of different investigators, is in excellent agreement with the value 0.1263 v. found by Carmody, and with the corrected values of Gerke (0.1264 v.) and Randall and Cann (0.1263). It is evident, therefore, that the present accepted[1] value of E^0_{Pb} (0.122 v.) is too low, and that the most reliable value is very close to 0.1263 v.

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[9] H. S. Harned and W. J. Hamer, THIS JOURNAL, **57**, 33 (1935).

[10] J. Shrawder, Jr., I. A. Cowperthwaite, and V. K. La Mer, *ibid.*, **56**, 2348 (1934).

[11] Private communication, submitted to THIS JOURNAL.

[12] H. D. Crockford and D. J. Brawley, *ibid.*, **56**, 2600 (1934).

[13] I. M. Kolthoff and C. Rosenblum, *ibid.*, **55**, 2656 (1933).

The Diazotization of Picramide

BY WARREN C. LOTHROP

During further investigations of the coupling of 5-hydroxy-6-methylhydrindene[1] with diazotized amines it seemed of interest to use diazotized picramide. The diazonium solution obtained by the method recently described by de Milt and van Zandt,[2] however, gave no reaction and therefore their reported coupling with β-naphthol was repeated. The compound formed with this reagent had the properties ascribed to it by the authors: a relatively low melting point (147°), which, however, could be raised by repeated crystallization from acetic acid to 155°; remarkable solubility in common solvents, and, in addition, extreme solubility in cold dilute alkali. The latter seemed particularly significant since it was shown long ago[3] that azo compounds formed by the coupling of β-naphthol are usually insoluble in alkali.

The coupling of diazotized picramide with β-naphthol also has been reported by Schoutissen,[4] but the azo compound which this investigator obtained had properties very different from those given above. It melted at 260°, was insoluble in most common solvents, and dissolved in alkali only with decomposition.

It seemed possible that the product obtained by the newer method might in reality be the molecular addition compound previously prepared by Witt[5] and noted by Misslin.[6] This was found to be the case. A sample was prepared from equimolecular quantities of β-naphthol and picramide and analyzed: (calcd. for $\mathrm{C_{16}H_{12}O_7N_4}$: N, 15.05. Found: N, 14.67). This bright red compound (m. p. 161–162°) when mixed with the disputed product (m. p. 155°) melted at 155–157°, and was indistinguishable from it in other respects.

These results explain the observed discrepancy and lead to the conclusion that the new method outlined by de Milt and van Zandt for the di-

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[1] Fieser and Lothrop, *ibid.*, **59**, 945 (1937).

[2] De Milt and van Zandt *ibid.*, **58**, 2044 (1936).

[3] Liebermann, *Ber.*, **16**, 2858 (1883).

[4] Schoutissen, THIS JOURNAL, **55**, 4533 (1933).

[5] Witt, *Ber.*, **41**, 3093 (1908).

[6] Misslin, *Helv. Chim. Acta*, **3**, 636 (1920).