and $v$ the molal volume of a pure component. The actual molal volumes, $V$, of the solutions are given by the relation

$$V = (N_1M_1 + N_2M_2)/d \qquad (3)$$

in which $M$ is a molar weight and $d$ the observed density. The expansions on mixing, $V - V_a$, recorded in column 6 of the table are zero almost within the limits of precision of the density determinations, *i. e.*, $\pm 1 \times 10^{-5}$. Consequently, if this expansion is assumed to be negligible, equations (2) and (3) may be combined to give the following simple relation between $N_{D_2O}$ and $\Delta S$

$$N_{D_2O} \doteq \alpha \Delta S/(1 - \beta \Delta S) \qquad (4)$$

in which

$$\alpha = M_1/M_2(1 - d_1/d_2) \doteq 9.235$$
$$\beta = [M_2d_1/d_2 - M_1]/M_2(1 - d_1/d_2) = 0.0309.$$

Evaluation of $\alpha$ and $\beta$ from the data of Table I by the method of least squares gives $\alpha = 9.2351$ and $\beta = 0.0327$, and since these constants reproduce the densities within the experimental uncertainties, as is shown by a comparison of columns 4 and 5, their use is recommended.

The author wishes to thank Dr. D. A. MacInnes for many helpful suggestions in connection with this work.

## Summary

The densities at 25° of a series of mixtures of light and heavy water have been determined. Contrary to the conclusion of earlier workers the components mix without appreciable change of volume. This fact is used in obtaining a new formula relating the composition of the mixtures to their densities.

NEW YORK, N. Y. RECEIVED JUNE 4, 1937

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SMITH COLLEGE]

# The Potential of the Ag(s), AgI(s), $I^-$ Electrode[1]

BY JESSIE Y. CANN AND ALICE C. TAYLOR

The purpose of this investigation was to determine, by means of electromotive force measurements, the potential of the Ag(s), AgI(s), $I^-$ electrode.

A search of the literature revealed that the results obtained for the value of this electrode were not concordant.[2]

## Method and Apparatus

In this investigation the cell

$$\mathrm{Ag(s),\ AgCl(s),}\ m\ \mathrm{KCl(aq.),}\ m\ \mathrm{KI(aq.),\ AgI(s),\ Ag(s)}$$

with flowing junction, was measured. Two pieces of apparatus were used: (1) that of MacInnes and Yeh,[3] and (2) that of Cann and Mueller,[4] suggested by the work of Randall and Cann.[5] In each case care was taken to prevent the flow of liquid over the electrodes.[6]

The cell was placed in the usual oil thermostat, regulated at 25°, and measurements were made with a shielded Leeds and Northrup Type K potentiometer.

## Materials

All solutions were made up by weight, moles per 1000 g. of water in vacuum, from high grade "analyzed" salts and conductivity water. Care was taken to remove all traces of oxygen by bubbling an inert gas through the solutions.

The Ag(s), AgCl(s) spiral electrodes were made according to the method of Randall and Young.[7]

The Ag(s), AgI(s) spiral electrodes were made by two different methods: first, electrolytically following the general method of Randall and Young,[7] electrolyzing the reduced silver spirals in a 0.05 normal solution of hydriodic acid, with a current of 0.005 ampere, for two hours; and, second, by heating to 650°, the silver spirals covered with a paste of one part silver iodate and nine parts silver oxide, for ten minutes in accordance with the second method of Owen.[2e] Both sets of electrodes were protected, as much as possible, from light. After being washed in distilled water, each set was short-circuited together for some hours. Immediately before being introduced into the cell

---

(1) The experimental part of this paper is a portion of a thesis submitted by A. C. Taylor in partial fulfilment of the requirements for the degree of Master of Arts at Smith College.

(2) (a) Noyes and Freed, THIS JOURNAL, **42**, 476 (1920); (b) Gerke, *ibid.*, **44**, 1684 (1922); (c) Pearce and Fortsch, *ibid.*, **45**, 2852 (1923); (d) Hass and Jellinek, *Z. physik. Chem.*, **162**, 153 (1932); (e) Owen, THIS JOURNAL, **57**, 1526 (1935).

(3) MacInnes and Yeh, *ibid.*, **43**, 2563 (1921).

(4) Cann and Mueller, *ibid.*, **57**, 2525 (1935).

(5) Randall and Cann, *ibid.*, **52**, 589 (1930).

(6) Carmody, *ibid.*, **54**, 210 (1932); Cann and LaRue, *ibid.*, **54**, 3456 (1932).

(7) Randall and Young, *ibid.*, **50**, 989 (1928).

the electrodes were placed in the particular solution to be used and evacuated for about thirty minutes, with gentle heating, to make sure of the complete removal of all oxygen. We found no appreciable differences in electrodes prepared by the two methods.

## Experimental Results

All determinations were made at 25°. Five different molalities of potassium chloride and potassium iodide were used as the flowing electrolytes. Table I gives the average values for at least ten cell readings for each concentration. Deviations from the average never exceeded ±0.0003 v. The liquid junctions were calculated according to Lewis and Sargent.[8] The values for the individual ion conductances were taken from the "International Critical Tables."[9]

TABLE I

| Molality of KCl and KI | E. m. f. at 25°, v. | Liquid junction $\pi$, v. | E. m. f. $-\pi$, v. | E. m. f. Ag, AgCl, v. | E. m. f. Ag, AgI, v. |
|---|---|---|---|---|---|
| 1.000 | −0.3723 | 0.0007 | −0.3730 | −0.2368 | 0.1362 |
| 0.500 | − .3724 | .0006 | − .3730 | − .2514 | .1216 |
| .100 | − .3725 | .0004 | − .3729 | − .2883 | .0846 |
| .050 | − .3728 | .0002 | − .3730 | − .3045 | .0685 |
| .005 | − .3724 | .0001 | − .3725 | − .3603 | .0122 |

In order to determine the potential of the silver–silver iodide electrode from the cell readings, it is necessary to know the potential of the silver–silver chloride electrode for each dilution. This value is calculated for each concentration by means of the equation

$$E = E^0 - \frac{RT}{F} \ln \frac{1}{\gamma m}$$

in which $\gamma$ equals the activity coefficient of potassium chloride, and $E^0$ for silver chloride is taken as −0.2223 v.[10] The activity coefficients are taken from the data of Hass and Jellinek.[2d]

The value of $E^0$ for the silver–silver iodide electrode was calculated from the values listed in Table I. Since the electrode reaction is

$$Ag(s) + I^- = AgI(s) + e$$

we may write

$$E = E^0 - \frac{RT}{F} \ln \frac{1}{aI^-} = E^0 - \frac{RT}{F} \ln \frac{1}{(m\gamma)I^-}$$

By subtraction of $(RT/F)\ln m$ from both sides of the equation we obtain

$$E - \frac{RT}{F} \ln m = E^0 - \frac{RT}{F} \ln \frac{1}{\gamma I^-}$$

At infinite dilution the activity coefficient is equal to one, and the last term drops out; thus

$$E - (RT/F) \ln m = E^0$$

We therefore determine $E^0$ by plotting $E - (RT/F) \ln m$, *i. e.*, $E - 0.05915 \log m$ against the molality and extrapolating the curve to infinite dilution. The values so determined are listed in Table II. From the plot of these values $E^0$ was taken as +0.1510.[11] This gives $\Delta F^0 = -3485$ cal.

TABLE II

| Molality of KI | E. m. f. Ag, AgI, v. | 0.05915 log *m*, v. | E. m. f. −0.05915 log *m*, v. |
|---|---|---|---|
| 1.000 | 0.1362 | −0.0000 | −0.1362 |
| 0.500 | .1216 | − .0178 | − .1394 |
| .100 | .0846 | − .0592 | − .1438 |
| .050 | .0685 | − .0770 | − .1455 |
| .005 | .0122 | − .1361 | − .1483 |

## Discussion of Results

Noyes and Freed[2] measured the cell

$H_2$(p. atm.), HI(xm), AgI(s), Ag(s)

from which they found the value of $E^0$ for the silver–silver iodide electrode to be +0.14773. Pearce and Fortsch[2] measured the same cell over a wider range of concentrations of hydriodic acid, and from their data $E^0$ may be calculated as +0.151, which is the value recorded in "International Critical Tables"[9] (Vol. VII, p. 332). Owen[2] has recalculated these values, using different assumptions as to the nature of the activity coefficients of hydriodic acid and finds from the data of Noyes and Freed[2] $E^0$ = +0.1527 and +0.1509; and from the data of Pearce and Fortsch $E^0$ = +0.1523, +0.1522, +0.1512 and +0.1507. Owen[2] has measured the cell

$H_2$, $HBO_2(m_1)$, $NaBO_2(m_2)$, KI(*m*), AgI(s), Ag(s)

TABLE III

| Date | Investigators | $E^0$, v. | Reference electrode |
|---|---|---|---|
| 1920 | Noyes and Freed | +0.14773 | Pt, $H_2$, $H^+$ |
| 1923 | Pearce and Fortsch | + .151 | Pt, $H_2$, $H^+$ |
| 1932 | Hass and Jellinek | + .1487 | Hg, HgCl, KCl (0.1 *N*) |
| 1935 | Owen | + .15219 | Pt, $H_2$, H (buffer) |
| 1936 | Cann and Taylor | + .1510 | Ag, AgCl, $Cl^-$ |
| | | $E^0$, v. (calcd.) | |
| 1935 | Owen | +0.1527 (N. & F.) | |
| | | + .1509 (N. & F.) | |
| | | + .1523 (P. & F.) | |
| | | + .1522 (P. & F.) | |
| | | + .1512 (P. & F.) | |
| | | + .1507 (P. & F.) | |

---

[8] Lewis and Sargent, THIS JOURNAL, 31, 363 (1909).

[9] "International Critical Tables," McGraw-Hill Book Co., Inc., New York City, 1930, Vol. VI, pp. 234–235.

[10] Harned and Ehlers, THIS JOURNAL, 55, 2179 (1933).

[11] By another method of extrapolation, *i. e.*, by plotting the observed e. m. f. values against the molality and making proper corrections, the value of $E^0$ is 0.1507. In this case the values in the most dilute solutions are given little weight.

He obtains $E^0 = +0.15219$ at 25°. Hass and Jellinek[2] have measured the cell

Ag(s), AgI(s), KI(satd.), KCl(satd.), KCl(0.1 *N*), HgCl(s), Hg

using the salt bridge in an attempt to eliminate the liquid junction. By extrapolation of their data $E^0 = 0.1487$.

Values calculated from these various data are summarized in Table III.

We take as our value +0.1510, from which $\Delta F^\circ = -3485$ cal.

## Summary

The cell

Ag(s), AgCl(s), *m* KCl(aq.), *m* KI(aq.) AgI(s), Ag(s)

was investigated.

The normal electrode potential of Ag(s), AgI(s), $I^-$ was found to be $E^0 = +0.1510$ and $\Delta F^\circ = -3485$ cal.

NORTHAMPTON, MASS. RECEIVED MARCH 30, 1937

---

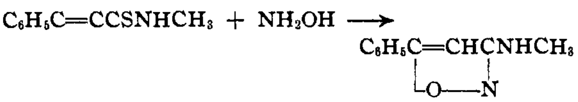
[CONTRIBUTION FROM PEARSON MEMORIAL LABORATORY, TUFTS COLLEGE]

# Further Observations on Acetylenic Thioamides

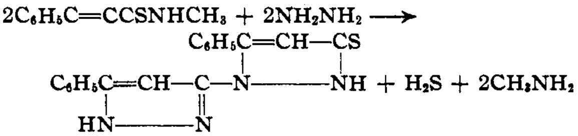
BY DAVID E. WORRALL

The thioamide obtained by the interaction of phenylacetylene and phenyl isothiocyanate possesses unusual properties because of the presence of the acetylenic group.[1] The present communication is concerned with the similar compounds prepared from mustard oils containing an aliphatic group.

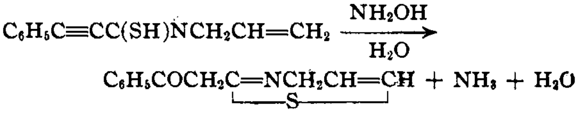
Methyl and allyl isothiocyanates, typical substances of the latter class, react quite smoothly with phenylacetylene although the products are lower melting and therefore less tractable than the corresponding anilide. The allyl derivative decomposes spontaneously on standing. Most conspicuous of the differences is the non-appearance of polymers, so characteristic of the other series. Heterocyclic ring formation tends to take place with the appropriate reagents although the transformation may be obscured by other changes. With hydroxylamine phenylpropiol-thiomethylamide (I) forms the usual type of isoxazole.



With hydrazine it gives a substance which contains sulfur, which cannot be the expected pyrazole, and which, moreover, is also obtained from phenylpropiol thioallylamide (II). It is probably a bicyclic derivative (III) resulting by further condensation.



The crude isoxazole obtained from II frequently contains a sulfur derivative. A similar result occurs in the case of thioanilides and has been[1] attributed to thiazole formation. It is well established that compounds or combinations containing allyl and thioamide groups are readily converted into penthiazoline derivatives. Accordingly,[2] the substance isolated from the isoxazole mixture may be regarded as a penthiazole (IV) resulting from the oxidation and hydrolysis of the enol of II or its addition product with hydroxylamine.



## Experimental

**Phenylpropiol Thiomethylamide (I).**—To 0.25 gram mole of phenylacetylene, converted into the sodium derivative and suspended in dry ether, was added the equivalent amount of methyl isothiocyanate. As heat sufficient to cause vigorous boiling was evolved, the mixture was cooled. It was worked up in the customary manner[1] after standing for several hours, except that the use of acid was unnecessary in precipitating the product; approximate yield of crude product, 31 g. No good solvent for purifying the substance was found, since decomposition occurred even on moderate heating. It was purified in small amounts by cooling with ice a saturated alcoholic solution prepared at room temperature and adding water a few drops at a time. Oils formed at first, but eventually there separated slender yellow needles melting with partial decomposition at 78–80°.

*Anal.* Calcd. for $C_{10}H_9NS$: C, 68.6; H, 5.1. Found: C, 69.1; H, 5.3.

Heating an alcoholic solution of I with or without alkali gave no indication of the formation of polymers. Among

---

[1] Worrall, THIS JOURNAL, **59**, 933 (1937).

[2] Dixon, *J. Chem. Soc.*, **69**, 24 (1896).