## Summary

In this paper are described determinations of the equilibrium of the reaction Se(black) + $2I_2(s)$ + $3H_2O$ = $H_2SeO_3 + 4H^+ + 4I^-$ at 25°. The equilibrium constant $K = (H_2SeO_3)(H^+)^4(I^-)^4$ was found to be $1.46 \times 10^{-14}$, expressing the concentrations in moles per 1000 g. of water and using the activities of $H^+$ and $I^-$ in place of their concentrations.

From this constant and existing thermodynamic data the reduction potential of Se(black) + $3H_2O(l)$ = $H_2SeO_3 + 4H^+ + 4E^-$ was calculated to be −0.740 volt, showing that the reducing power of selenium (at 1 *M* $H^+$ concentration) is about the same as that of $Fe^{++}$, $Fe^{+++}$ (−0.747), and intermediate between those of $I^-$, $I_2(s)$ (−0.536) and Ag, $Ag^+$ (−0.800).

The corresponding free energies ($\Delta F^\circ$) at 25° of $H_2SeO_3$, $HSeO_3^-$, and $SeO_3^=$ at 1 *M* were found to be −101,360, −97,850 and −87,890 calories, respectively.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE NON-RESIDENT LECTURESHIP IN CHEMISTRY, BAKER LABORATORY, CORNELL UNIVERSITY]

# TRANSITION CELLS OF THE SIXTH CLASS

BY ERNST COHEN AND ERNEST J. JOSS

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A transition cell may be defined broadly as any reversible galvanic element containing a solid substance which may exist in a number of modifications.

While five different classes of such elements have been treated theoretically as well as experimentally by Ernst Cohen and his co-workers,[1] transition cells of the sixth class have not, as yet, been experimentally realized. Such an element is to contain a depolarizer which possesses a transition point. This paper deals with a transition cell of this type, the depolarizer being silver iodide.

## Experimental

It was thought best to use a cell with a standard electrode, rather than two electrodes of silver iodide, one stable and the other metastable. With the former type of cell the temperature-e.m.f. curve may be run over a wide range of temperatures, the transition temperature being indicated by a sudden change in the temperature coefficient of e.m.f. The choice of an electrolyte afforded some difficulty. The use of aqueous solutions was impractical, since the temperatures to be used were as high as 175°. The solvent finally chosen was fused calcium chloride hexahydrate. The boiling point of this substance was within the temperature range over

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[1] Ernst Cohen, "Physico-chemical Metamorphosis and Some Problems in Piezochemistry," McGraw-Hill Book Co., New York, 1926, p. 151 ff.

which the experiments were to be run, so a closed apparatus was necessary. The melting point was 29.9° which was well below all experimental temperatures.

The cells were made up according to the following scheme:

$$\mathrm{Ag}_{(s)} - \mathrm{AgI}_{(s)} \left| \begin{array}{c} \mathrm{CaCl_2.6H_2O}_{(l)} \\ \mathrm{AgI}_{(c_1)} \\ \mathrm{PbI}_{2(c_2)} \end{array} \right| \mathrm{Pb}_{(s)}$$

The design of the cell is shown in Fig. 1.

A, the positive pole, is a silver iodide electrode made after the method of Jones and Hartmann.[2] B is the standard electrode, made of pure lead. The two electrodes were joined to the H-cell by means of inner seals. A side tube was provided for introducing the electrolyte. The whole cell, made of heavy Pyrex glass, was quite small and compact.

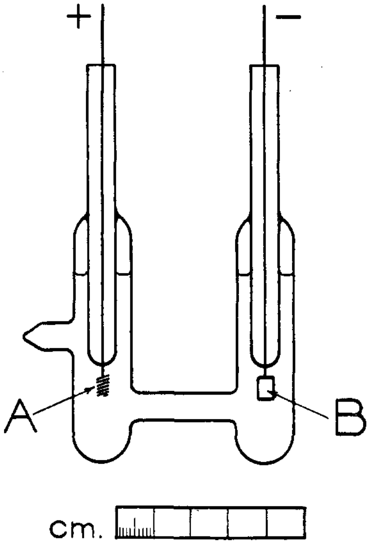

Fig. 1.

The electrolyte was molten calcium chloride hexahydrate saturated with both silver iodide and lead iodide at 40°. This solution was introduced into the cell through the side tube, which was subsequently sealed off at a constriction provided for this purpose. It is probable that little if any silver iodide was in solution around the lead electrode, due to interaction with the metallic lead.

The cell was completely immersed in a bath of Crisco, a hydrogenated cooking fat. This bath was placed in an air thermostat for temperature control. The air thermostat was built from an ordinary 50 × 45 × 30 cm. gas oven. This was covered on all sides with a 2 cm. layer of sheet asbestos. Air circulation was maintained within the oven by means of a 20cm. four bladed fan. The shaft driving this fan ran in a bearing fastened in a board across the top of the oven. The fan was driven at about 1400 r.p.m. by a small electric motor. A separate motor ran a stirrer for the oil-bath. The stirrer passed through the top of the oven and was connected directly to the motor. The speed of this motor was approximately 200 revolutions per minute.

The temperature of the oven was controlled by means of a spiralled, mercury in glass, thermal regulator. The capillary tube at the top of the regulator was passed through the top of the oven and protruded eight centimeters up into the outside air. This precluded the dangers of mercury at high temperatures. The temperature was measured by means of a thermometer immersed in the oil-bath, so that the mercury bulb was very close to the transition element. The thermometers used were very long so that the scale was visible above the oven. These thermometers were graduated with 0.1° divisions and calibrated against standard thermometers calibrated by the Physikalisch-Technische Reichsanstalt at Charlottenburg-Berlin.

The oven was fitted with a main electrical heating unit, consisting of a number of coils of nichrome wire wound on Pyrex glass tubes, and an auxiliary heating unit made by winding a single coil of nichrome wire on asbestos board. One end of the main

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[2] Jones and Hartmann, This Journal, **37**, 755 (1915).

heating coil was attached to one end of the auxiliary coil, from which junction a common lead was run to the source of current (110 A.C.). The other end of the main heating coil was connected, in series with a variable rheostat (Ward-Leonard, Type RLR 155) and an ammeter (Weston, 10-ampere range, with 1.5 multiplier), to the source of current. The other end of the auxiliary coil was connected, in series with a fixed resistance and a relay, to the source of current. Both circuits were equipped with knife switches so that they might be operated independently. The relay in the auxiliary circuit was governed by the mercury thermo-regulator and a four-volt source of current. The resistances were fixed so as to cause the main heating coil alone to raise the temperature to about five degrees below the desired temperature; while the auxiliary coil, if the circuit were kept closed, would further raise the temperature to about five degrees above that desired.

The leads from the transition cell were carried out through small glass tubes passing through the side of the oven.

The vibration of the stirrers increased the sensitivity of the thermo-regulator markedly.

With the thermostat described above, temperatures constant to within 0.1° for long periods of time were obtainable.

The electromotive force of the cell was measured by means of the Poggendorff compensation method. A Leeds and Northrup student potentiometer was used in connection with a quite sensitive galvanometer. The standard of electromotive force was a Weston cell.

The method used was to start measurements at the lower end of the temperature range and so regulate the current through the main heating element as to have the temperature rise approximately one degree centigrade every five minutes. The electromotive force was measured for every half degree rise in temperature, the potentiometer being balanced against the standard cell every few readings. When the temperature had risen as high as was desired, the current was so adjusted as to allow cooling at the same rate as the heating. Measurements were again made in the same manner as with rising temperature.

The cell came to equilibrium very rapidly under the conditions of the experiment. This was proved by the fact that the electromotive forces measured with rising temperature checked those with falling temperature within experimental error.

Each of the two runs shown in the following tables was completed without interruption. A different cell was used in each run.

Table I gives the data for the first cell, which we shall designate as Cell I. In this table $t$ refers to the actual temperature in centigrade degrees and $E$ to the electromotive force of the cell in volts. The points indicated by asterisks are those arbitrarily chosen for calculations.

TABLE I

DATA FOR CELL I

| $t$ | $E$ | $t$ | $E$ | $t$ | $E$ | $t$ | $E$ |
|---|---|---|---|---|---|---|---|
| 128.07 | 0.2599 | 129.41 | 0.2603 | 141.40 | 0.2670 | 152.00 | 0.2724 |
| 120.33 | .2556 | 129.82 | .2605 | *141.97 | .2673 | *152.70 | .2726 |
| 117.91 | .2543 | 130.30 | .2607 | 142.82 | .2678 | 154.00 | .2731 |
| 120.90 | .2558 | *130.70 | .2610 | 143.31 | .2682 | 154.75 | .2735 |
| 118.70 | .2547 | 131.31 | .2613 | *144.30 | .2687 | 155.40 | .2738 |
| 119.47 | .2555 | 131.95 | .2616 | 145.10 | .2691 | *155.95 | .2740 |

TABLE I (*Concluded*)

| | E | | E | | E | t | E |
|---|---|---|---|---|---|---|---|
| 119.62 | .2557 | 132.78 | .2621 | 145.79 | .2695 | 156.55 | .2743 |
| 121.50 | .2560 | 133.38 | .2625 | 146.19 | .2698 | 157.10 | .2745 |
| 122.07 | .2563 | 134.42 | .2630 | 146.90 | .2701 | 157.65 | .2747 |
| 122.93 | .2567 | 135.25 | .2634 | *134.28 | .2631 | *158.20 | .2750 |
| 123.50 | .2570 | 135.80 | .2637 | 144.70 | .2687 | 159.00 | .2753 |
| *124.13 | .2573 | 136.25 | .2640 | 145.75 | .2694 | *159.25 | .2756 |
| 124.71 | .2576 | 136.80 | .2643 | 146.38 | .2698 | 161.20 | .2762 |
| 125.35 | .2579 | *137.30 | .2646 | 146.90 | .2701 | *161.80 | .2765 |
| 125.78 | .2582 | 137.97 | .2650 | *147.30 | .2705 | 167.80 | .2794 |
| 126.29 | .2585 | 138.32 | .2653 | *149.00 | .2710 | 167.70 | .2794 |
| 126.72 | .2588 | 139.00 | .2656 | 149.50 | .2712 | 168.18 | .2795 |
| 127.20 | .2590 | 139.62 | .2660 | 150.60 | .2716 | 169.20 | .2803 |
| 127.80 | .2594 | 140.12 | .2663 | 150.80 | .2718 | 169.60 | .2810 |
| *128.28 | .2596 | 140.70 | .2666 | 151.17 | .2720 | | |

These data when plotted give the graph shown in Fig. 2. The ordinates are electromotive forces in volts and the abscissas are temperatures in centigrade degrees.

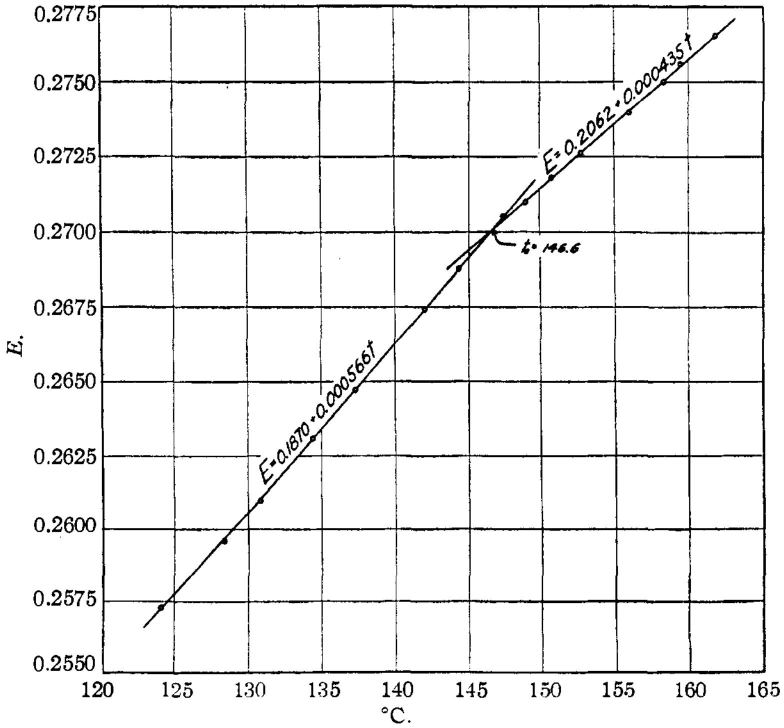

Fig. 2.

It may be seen that the temperature coefficient of e.m.f. is constant over two distinct ranges of temperature. The intersection of the two curves gives the transition temperature. To find this temperature accurately it was necessary to calculate the equation for each of the two curves, using the method of least squares, and to solve for the point of intersection. The equation of the lower curve, which we shall call the $\alpha$-curve, since the $\alpha$-form of silver iodide is stable in this range, is

$$E_1 = 0.1870 + 0.000566\ t \tag{1}$$

The equation of the upper curve, which we shall designate as the $\beta$-curve, is

$$E_2 = 0.2062 + 0.000435\ t \tag{2}$$

The intersection of these curves is found to be at 146.6°. This is the transition temperature of $\alpha$- and $\beta$-silver iodide.

Table II shows the results obtained with Cell II. The asterisks indicate the points upon which calculations were based.

TABLE II

DATA FOR CELL II

| *t* | *E* | *t* | *E* | *t* | *E* | *t* | *E* |
|---|---|---|---|---|---|---|---|
| 115.90 | 0.2363 | 132.50 | 0.2440 | 146.90 | 0.2515 | *155.80 | 0.2545 |
| 116.28 | .2365 | *133.10 | .2444 | 147.60 | .2518 | 155.30 | .2543 |
| 116.70 | .2368 | 134.12 | .2448 | *148.02 | .2520 | *154.50 | .2540 |
| 117.32 | .2370 | 134.68 | .2451 | 148.70 | .2523 | 154.20 | .2538 |
| 118.10 | .2373 | 135.95 | .2458 | 149.30 | .2525 | *153.00 | .2535 |
| 119.16 | .2377 | *136.43 | .2460 | 150.40 | .2528 | *152.20 | .2533 |
| 119.80 | .2380 | 137.10 | .2463 | 151.92 | .2533 | 151.55 | .2530 |
| 120.30 | .2383 | 137.30 | .2465 | 152.20 | .2535 | *150.60 | .2526 |
| 120.69 | .2385 | 138.00 | .2468 | 153.00 | .2538 | 150.35 | .2525 |
| 121.38 | .2388 | *138.35 | .2470 | 153.70 | .2540 | *149.45 | .2522 |
| 121.67 | .2390 | 139.30 | .2473 | 154.60 | .2543 | *148.80 | .2520 |
| 122.33 | .2393 | *139.80 | .2476 | 155.30 | .2545 | 147.85 | .2518 |
| 122.80 | .2395 | 140.56 | .2480 | 156.13 | .2548 | 147.05 | .2515 |
| 123.98 | .2400 | 141.10 | .2483 | 156.55 | .2550 | 146.90 | .2510 |
| 124.72 | .2403 | 141.40 | .2485 | 156.98 | .2551 | 146.55 | .2513 |
| *125.07 | .2405 | 141.90 | .2488 | 158.20 | .2555 | 145.95 | .2510 |
| 126.03 | .2410 | 142.32 | .2490 | *158.80 | .2558 | 145.48 | .2508 |
| 126.71 | .2413 | 142.90 | .2493 | 159.55 | .2560 | 144.50 | .2500 |
| 127.02 | .2415 | *143.40 | .2495 | *160.30 | .2562 | 143.68 | .2497 |
| 127.70 | .2418 | 143.89 | .2498 | 161.00 | .2564 | 142.50 | .2492 |
| 128.62 | .2422 | 144.30 | .2500 | 159.80 | .2560 | 141.80 | .2483 |
| *129.78 | .2427 | 144.90 | .2503 | 159.30 | .2559 | 141.02 | .2480 |
| 130.23 | .2430 | 145.20 | .2505 | 158.50 | .2555 | 139.82 | .2474 |
| 130.80 | .2433 | *145.70 | .2508 | 157.95 | .2553 | | |
| 131.31 | .2435 | 145.91 | .2510 | *157.00 | .2550 | | |
| *132.00 | .2438 | 146.50 | .2513 | 156.55 | .2548 | | |

The equation of the $\alpha$-curve, the one along which $\alpha$-silver iodide is stable, is

$$E_1 = 0.1775 + 0.0005026\ t \tag{3}$$

The equation of the $\beta$-curve is

$$E_2 = 0.1968 + 0.000371\ t \tag{4}$$

The intersection of the two curves is found to be at 146.7°.

The transition temperature of silver iodide will be treated by us in a special paper. Suffice it to say here that the values mentioned in the earlier literature vary from 138 to 147°. This is a consequence of the strong retardations which may occur in this transition. In our case evidently there occurred no retardation, the electrolyte acting as an accelerator.

It is of interest to know the heat of transition of silver iodide. If we write this reaction, assumed to be occurring in the cell below the transition temperature, we have:

$$\mathrm{AgI}_\alpha + {}^1/_2\mathrm{Pb} = \mathrm{Ag} + {}^1/_2\mathrm{PbI}_2 \qquad (5)$$

The reaction assumed to be occurring above the transition temperature is:

$$ {}^1/_2\mathrm{PbI}_2 + \mathrm{Ag} = \mathrm{AgI}_\beta + {}^1/_2\mathrm{Pb} \qquad (6)$$

The summation of the two reactions gives

$$\mathrm{AgI}_\alpha = \mathrm{AgI}_\beta \qquad (7)$$

At the transition temperature, the two forms of silver iodide are in equilibrium, hence the free energy increases of the two reactions are equal, that is

$$\Delta F_5 = \Delta F_6 \qquad (8)$$

where the subnumerals refer to the marginal numbers of the equations. The increase in heat content for the transition as expressed by Equation (7) is given by the following equation

$$\Delta H_7 = TNf\left[\frac{dE_5}{dT} + \frac{dE_6}{dT}\right], \qquad (9)$$

where $T$ is the temperature of transition on the absolute scale, $N$ is the valence change, $f$ is Faraday's constant and $E$ is the electromotive force of the cell.

Let us now apply this equation to the data of Cell I. From (1) and (2)

$$\Delta H_7 = 419.6 \times 1 \times 96{,}500\ (0.000566 - 0.000435)$$
$$\Delta H_7 = 5304 \text{ joules} = 1267 \text{ cal. per gram mole}$$

The same calculation for Cell II (from 3 and 4) gives

$$\Delta H_7 = 419.7 \times 1 \times 96{,}500\ (0.0005026 - 0.000371)$$
$$\Delta H_7 = 5330 \text{ joules} = 1274 \text{ cal. per gram mole}$$

The average of these two values is 1270 cal., that is

$$\mathrm{AgI}_\alpha = \mathrm{AgI}_\beta - 1270 \text{ cal.}$$

Previous determinations by various investigators vary from 1355 to 1597 cal.

## Summary

1. A type of transition cell pointed out by one of us many years ago, but hitherto never experimentally realized, has been constructed.

2. This transition cell of the sixth class, in which the depolarizer undergoes a polymorphic transformation, is experimentally realized in the case of silver iodide.

3. Temperature-e.m.f. measurements show the transition temperature to be 146.6°.

4. The heat absorbed during transition of one mole of $AgI_\alpha$ to one mole of $AgI_\beta$, calculated from the slopes of the e.m.f.-temperature curves, is 1270 cal.

ITHACA, NEW YORK

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

# DECOMPOSITION OF DIACETONE ALCOHOL BY WEAKER BASES

BY GÖSTA ÅKERLÖF

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## Introduction

In two preceding papers[1] have been given the results of the measurements of the decomposition velocity of diacetone alcohol in alkali hydroxide-alkali salt solutions. In this paper will be presented some measurements with weaker bases, such as ammonia, used as catalysts. Similar measurements for hydrogen ion catalysis with weaker acids present have been carried out by Harned and Hawkins[1c] for the hydrolysis of ethyl formate and ethyl acetate.

Previously it has been shown by Arrhenius,[2] Brönsted,[3] Harned[1] and others,[4] that when a neutral salt, which in itself is a strong electrolyte, is added to a solution of a weak electrolyte, the dissociation of this increases. For water as a weak electrolyte this increase has been measured by Harned[4a,b] Harned and Swindells,[5] Åkerlöf,[6] and Harned and James[7] for a number of different salt solutions. At low salt concentrations the curves obtained for the decomposition velocity of diacetone alcohol in neutral salt solutions of the weaker bases seemed to be of the same type as the curves obtained for the concentration of water as an electrolyte in the same salt solutions. In other words, the concentration of the weak bases as electrolytes was changed by the addition of neutral salts in the same manner as for water.

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[1] (a) Åkerlöf, THIS JOURNAL, **48**, 3046 (1926); (b) **49**, 2955 (1927); (c) Harned and Hawkins, *ibid.*, **50**, 85 (1928). They give references relating to older literature on this subject.

[2] Arrhenius, *Z. physik. Chem.*, **31**, 197 (1899).

[3] Brönsted, *J. Chem. Soc.*, **119**, 574 (1921).

[4] (a) Harned, THIS JOURNAL, **47**, 930 (1925); (b) *Z. physik. Chem.*, **117**, 1 (1925); compare further (c) Schreiner, *Z. anorg. Chem.*, **135**, 333 (1924); (d) Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

[5] Harned and Swindells, THIS JOURNAL, **48**, 126 (1926).

[6] Åkerlöf, *ibid.*, **48**, 1160 (1926).

[7] Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926).