that the lead chloride–lead bromide solid solutions would exhibit a discontinuity in chemical action at mole fraction 0.75 of lead chloride.

Summary

1. The energy changes of solid lead chloride upon dilution with lead bromide have been determined at mole fractions of lead chloride varying from 1 to 0.200, between the temperatures of 200 and 300°.

2. The solid solution containing 0.75 mole of lead chloride is shown to be the most stable.

3. The thermodynamic properties of these solutions are considered compatible with the existence of a regular arrangement of bromide ions in the lead chloride lattice.

4. A discontinuity in chemical action of the solid solutions at mole fraction 0.75 of lead chloride is predicted.

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A NEW USE OF THE VACUUM TUBE IN ELECTROMETRIC TITRATIONS. I. POLARIZATION OF PLATINUM ELECTRODES IN OXIDATION AND REDUCTION REACTIONS[1]

BY J. L. KASSNER, R. B. HUNZE AND J. N. CHATFIELD

Introduction

Since the advent of the radio it is generally known that electrons are drawn across the tube by means of a positive potential impressed on the plate. The plate current in the tube is controlled largely by means of a grid which is placed between the filament and the plate. If a positive potential is placed on the grid, electrons flow to the plate in greater number, and if a negative potential is placed on the grid fewer electrons will flow to the plate, lowering the plate current. Goode[2] utilized the fact that the grid will not pick up electrons when it is charged negatively with respect to the filament and connected the indicator electrode directly to the grid. This same principle has been employed by other investigators.[3] In all of the investigations reported, in which a single electron tube was employed, it has been necessary to plot $\Delta E/\Delta v$ or to plot galvanometer deflections in place of ΔE to obtain the equivalence point. Daniels, Mathews and

[1] Paper presented before the Buffalo meeting of the American Chemical Society.

[2] Goode, THIS JOURNAL, **44**, 26 (1922).

[3] Calhane and Cushing, *J. Ind Eng. Chem.*, **15**, 1118 (1923); Treadwell, *Helv. Chim. Acta*, **8**, 89 (1925); Williams and Whitenack, *J. Phys. Chem.*, **31**, 519 (1927).

Williams[4] state that the characteristics of a vacuum tube should always be determined before it is used for any purpose, and since the characteristics of a vacuum tube vary with the age of the tube as well as with new tubes of the same type, the application of vacuum tubes to electrometric titrations has not been widely adopted. This investigation was started to find, if possible, a method of utilizing the vacuum tube in electrometric titrations in such a way that the results of the titrations are less dependent upon the characteristics of the tube and to avoid the necessity of plotting curves to obtain the equivalence point. The following "hook-up" and data are presented as evidence of how well this has been accomplished. A diagram of the apparatus is shown in Fig. 1.

Fig. 1.—F and C, platinum electrodes, B. and S. No. 28 about 3 cm. long; P, shunt; V, voltmeter reading in units of 0.1 volt; D, potential divider; C, 4.5-volt C-battery; B, 22.5-volt B-battery; G, galvanometer of about 1000 ohm resistance; A in circle, milliammeter; W, 50-ohm variable resistance; R, 5000-ohm variable resistance; A, 6-volt storage battery. A motor-driven stirrer is not shown.

This apparatus differs from Goode's in that a positive potential is impressed on the grid of the vacuum tube; a Cunningham amplifier, 301A or R. C. A., 201 A, whose filaments operate normally at 6 volts, drawing 0.25 ampere; and the grid current has been employed to polarize bimetallic platinum electrodes which have been substituted for the monometallic system.   Part of the grid current (the grid current is very small because of the construction of the vacuum tube) is shunted around the electrodes.

When electrodes have been placed in the solution to be titrated and the resistance R adjusted so that the galvanometer reads zero; the points M and N are at the same potential.   Electrons are flowing through the tube in three distinct circuits: the filament, filament to grid, and filament to plate.   The electrons that are picked up by the plate may be considered as flowing through the B-battery, R, and back to the A-battery.   The strength of this current depends upon the temperature of the filament, the voltage of the B-battery, the value of R, and the potential impressed on the grid.   The current in the three circuits will remain constant during the course of a titration as long as the potential difference between F and C remains constant if the other adjustments are not changed.   A slight change in the potential between F and C will produce a corresponding

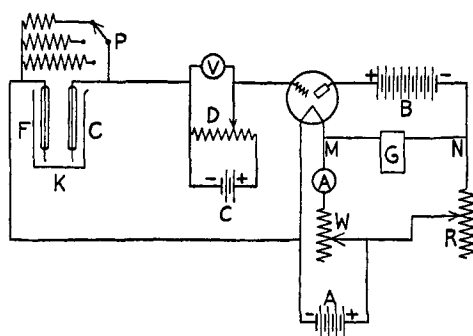⁴ Daniels, Mathews and Williams, "Experimental Physical Chemistry," McGraw-Hill Book Co., Inc., New York, 1929, p. 402.

change in the potential impressed on the grid. This will produce a relatively large change in the plate current, which will unbalance the system. M and N will no longer be at the same potential and the galvanometer will deflect.

Experimental

The theory of polarized electrodes has been studied in detail by Willard and Fenwick[5] and Van Name and Fenwick.[6] They have shown that polarized platinum electrodes owe their effect in electrometric titrations to gas reactions taking place on the surface of the electrodes and that the potential difference between the electrodes remains practically constant up to about 0.5 ml. of the equivalence point.

For the successful operation of this apparatus it is necessary for the potential difference between the electrodes to remain constant up to the equivalence point, and this has been accomplished by shunting part of the polarizing current around the electrodes. Shunted electrodes were first used by Foulk and Bawden.[7] They stated that no current flows through the solution when the drop in potential across the shunt is equal to the back e. m. f. due to polarization. For this reason it was thought that it would be necessary to control the shunt within narrow limits, but it was found that the shunt could be varied over a comparatively wide range without vitiating the results. The results of the titrations using different shunts are presented in Table I.

TABLE I

TITRATION OF APPROXIMATELY 0.1 N SODIUM THIOSULFATE WITH IODINE

V, 1.6 volts; filament current, 0.25 ampere; B-battery, 22.5 volts

Run	Calcd., ml.	Iodine Found, ml.	Error. ml.	Shunt P, ohms
1	25.15	25.13	0.02	20,000
2	25.15	25.12	.03	5,000
3	25.15	25.15	.00	35,000

No attempt was made to determine the absolute limits of the shunt. The calculated ml. are the average of three concordant determinations using starch as the indicator. When no shunt resistance was employed the needle of the galvanometer drifted off the scale after the addition of about 2 ml. However, it is possible to titrate with a shunt of infinite resistance if the correct voltage is impressed on the grid, but more difficulty is experienced in balancing the potentials. As is shown by the table, the end-point obtained by the electrometric method is slightly in advance of the end-point obtained by the starch indicator. Attention was also called to this fact by Foulk and Bawden.[8] It has been found that it is possible,

[5] Willard and Fenwick, THIS JOURNAL, **44**, 2504 (1922).

[6] Van Name and Fenwick, *ibid.*, **47**, 9, 19 (1925).

[7] Foulk and Bawden, *ibid.*, **48**, 2045 (1926).

[8] Foulk and Bawden, *ibid.*, **48**, 2047 (1926).

keeping the other conditions the same as those given in the table, to vary the shunt over the same range in the titrations of bichromate with ferrous ammonium sulfate, arsenite with bromate, and arsenite with iodine.

Reference to Fig. 1 shows that the potential impressed on the grid is less than the reading of the voltmeter, V, by the potential of the counter e. m. f. due to polarization. Since the plate current is a function of the potential impressed on the grid it can be seen why the system remains balanced up to the equivalence point if the potential difference between the electrodes remains constant, and then suddenly changes at the end-point. Table II is offered in support of the theory that the potential difference between the electrodes remains constant up to the equivalence point if the right conditions are employed. The slight fluctuations in the potential difference from 1 to 13.84 ml. are, undoubtedly, the result of experimental error.

TABLE II

POTENTIAL DIFFERENCE BETWEEN POLARIZED PLATINUM ELECTRODES IN THE TITRATION
OF SODIUM ARSENITE WITH POTASSIUM BROMATE

Ml. of 0.1 N KBrO₃	E. m. f. with respect to N-calomel electrode		F minus C, mv.	Galv., zero center
	C, cathode, mv.	F, anode, mv.		
0.00	284	529	245	0
1.00	270	527	257	2, left
6.00	269	525	256	3, left
12.00	266	525	259	6, left
13.40	268	528	260	8, left
13.70	269	529	260	9, left
13.80	266	525	259	10, left
13.83	262	527	265	10, left
13.84	359	622	263	12, left
13.85	679	872	193	Extreme right

In making these measurements a 50,000-ohm resistance was kept in series with the electrodes, but even then enough current was drawn from them, in the process of balancing, to change the potential of the electrodes slightly. In carrying out titrations in which the potential of the electrodes was not measured, the drift of the galvanometer needle was of less magnitude. The two additions of potassium bromate from 13.83 ml. to 13.85 ml. were made with the aid of a stirring rod, and the readings are offered merely to show that the change at the equivalence point is very sharp. The change is confined to within 0.05 ml. of 0.01 N solution in a volume of 250 to 300 ml.

The main objection offered to the use of polarized bimetallic electrodes is that the approach of the end-point is indicated only about 0.3 ml. in advance. This indication is far enough in advance for the successful use of this apparatus, because the operator has only to control the buret and

observe the galvanometer, since it is not necessary to make any adjustments after the titration is begun. Furthermore, this "hook-up" possesses an additional characteristic in that the indication of the approach can be controlled by placing the electrodes in the solution in such a position that there will be a slight difference in the composition of the solution surrounding one of them as the equivalence point is approached. This difference in composition will be only momentary due to the process of mixing. This will be manifested by a temporary instability of the galvanometer. The galvanometer again becomes stable if the addition of the titrating solution is discontinued. After the indication of the approach[9] of the end-point is obtained, the titration can be continued dropwise until the needle of the galvanometer "kicks" off the scale and remains there.[10]

If the operator does not wish to rely upon the indication of the approach in order to avoid overstepping the end-point, a small portion of the unknown solution can be withheld in a small dropper until the apparent end-point is obtained. Upon the addition of this small portion the needle will return to its former position. The end-point can then be approached dropwise.

In order to show that it is not necessary to control the different variables in this apparatus within narrow limits the following data are presented.

The Bichromate–Ferrous Iron Reaction.—The results of titrations with the apparatus described in this paper in comparison with those obtained with the Wendt electrometric titration apparatus are given in Table III.

[9] Best results are obtained when the standard solution is added at a constant rate of about 1 ml. in seven seconds up to this point.

[10] For three of the determinations (arsenite with iodine, arsenite with bromate, and thiosulfate with iodine) reported in this paper the optimum positions of the electrodes were found to be as follows. With the stirrer placed in the center and near the bottom of a 400-ml. beaker containing 200–250 ml. of solution, electrode F with the wire running in an almost horizontal position toward the back of the beaker was placed about 2 cm. above the stirrer and to the extreme right of the beaker. Electrode C was placed to the left of the stirrer with the wire running almost in a horizontal position toward the front of the beaker a little below the stirrer, the stirrer rotating in the direction of electrode F. The solution was added from a buret placed about 1 cm. to the left and about 1 cm. in front of the stirrer. If the indication of the approach of the end-point is given too soon it can be postponed by lowering electrode F, or if too late it can be advanced by raising elecctrode F. After a little experience the operator will have no difficulty in adjusting the electrodes so as to obtain an indication of the approach at the point he most desires. Although not necessary to do so, it has been found advantageous to reverse the relative positions of electrodes F and C in the titration of potassium bichromate with ferrous ammonium sulfate, for when the solution is thrown upon electrode C in this titration, the indication of the approach is obtained by the needle "kicking" left, whereas, in the other three titrations, "kicks" to the left were obtained when the solution was thrown upon electrode F. By left is meant the opposite direction to that in which the needle of the galvanometer goes at the end-point.

TABLE III

TITRATION OF APPROXIMATELY 0.1 N BICHROMATE WITH FERROUS SULFATE

| | | FeSO₄ | | | Current | | B- | | |
| | | Calcd., | Found, | Error, | Plate, | Filament, | battery, | V in | P in |
Run	Tube	ml.	ml.	ml.	Ma	Ampere	volts	volts	ohms
1	1	26.60	26.60	0.00	1.25	0.25	22.5	1.6	20,000
2	1	26.60	26.57	.03	0.65	.20	18.0	1.2	15,000
3	1	26.60	26.59	.01	2.50	.27	36.0	2.0	25,000
4	2	26.60	26.60	.00	2.10	.26	36.0	2.0	25,000
5	2	26.60	26.62	.02	0.51	.20	18.0	1.2	15,000

Initial volume, 200–250 ml.; deflection of galvanometer to extreme right.

In most cases the needle drifted five or more spaces to the left during the course of the titration. The calculated values are the average of several concordant determinations with the Wendt apparatus.

The following titrations were carried out and essentially the same results were obtained when the variables were varied as shown in Table III: sodium thiosulfate with iodine, sodium arsenite with iodine and with bromate. Other tubes of the same type but with different characteristics were used with equal success.

The conditions given in Run 1 of Table III have been selected as the optimum. No attempt was made to determine the exact limits of the different variables. Each variable can be varied independently over the following range if the other factors are left constant as given in Run 1: P, 5000–35,000 ohms; V, 0.4–2.2 volts; B, 18–45 volts; filament current, 0.18–0.27 ampere. These are not absolute limits.

Accuracy.—Approximately 0.01 N solutions were prepared by diluting the 0.1 N solutions employed above ten times and for this reason the calculated values of the 0.01 N have been considered numerically equal to those of the 0.1 N. Table IV gives the results of a typical titration.

TABLE IV

TITRATION OF APPROXIMATELY 0.1 N BICHROMATE WITH FERROUS SULFATE

	1	2	3
Ferrous sulfate, calcd. ml.	26.60	26.60	26.60
Ferrous sulfate, found ml.	26.64	26.62	26.65
Error, ml.	0.04	0.02	0.05

Total volume 200–250 ml.

When the galvanometer employed had a sensitivity of 0.5 microampere per millimeter, a deflection of only ten scale divisions was obtained with 0.01 N solutions but when a galvanometer which had a sensitivity of 0.025 microampere per millimeter was employed a deflection of more than thirty scale divisions per drop was obtained. The addition of one drop of 0.001 N iodine solution to a volume of 250 ml. of a slightly acid solution gave a deflection of twenty scale divisions with the latter galvanometer. Because of the extreme precautions that must be taken when working with 0.001 N

solutions it will be necessary to delay the report on this dilution until a later date.

Summary

1. A positive potential has been impressed upon the grid instead of the usual negative.

2. The polarization of platinum electrodes by means of a grid current has been used to advantage in the electrometric titrations of some oxidation–reduction reactions.

3. The different variables in this "hook-up" may be varied over a range of 20% without vitiating the results.

4. The equivalence point is indicated by the "kick" of a sensitive galvanometer and possesses the following characteristics: (a) approach is indicated, (b) high sensitivity, (c) over-stepping is immediately apparent, (d) the plotting and recording of readings is unnecessary, (e) tubes of the same type give the same equivalence point, (f) adjustments are unnecessary during titration.

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THE CLASSICAL DISSOCIATION CONSTANT OF BROMCRESOL GREEN, CHLORPHENOL RED AND METHYL RED IN POTASSIUM CHLORIDE SOLUTIONS[1]

BY ELWYN F. CHASE AND MARTIN KILPATRICK, JR.

A great part of the work in the colorimetric determination of hydrogen-ion concentration has been based on the incorrect assumption that equal color in solutions of equal indicator concentration meant equal hydrogen-ion concentration. That this assumption leads to errors of considerable magnitude has been clearly pointed out by Güntelberg and Schiödt.[2] They show that for the case studied by Szyszkowski[3] the error due to the above assumption amounted to several hundred per cent. Consequently, this error is of the greatest importance and a clear understanding of the factors involved is essential.

An indicator is nothing more than a weak acid, or base, where the acid form, or basic form, or both, is colored due to some structural rearrangement. Thus we can have a buffer system just as with any weak electrolyte

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[1] Abstracted from the thesis of Elwyn F. Chase presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1931.

[2] Güntelberg and Schiödt, Z. physik. Chem., 135, 393 (1928).

[3] Szyszkowski, ibid., 58, 420 (1907).