is the curve $K_2Si_2O_5 + KHSi_2O_5 + L + V$ (curve 4*b*), which goes from Q_4 to Q_5. The equation of this curve is

$$\frac{dp}{dt} = \frac{(\eta^l - \eta^v) + \frac{A_{1lv}}{A_{12l}}(\eta' - \eta^l) - \frac{A_{1lv}}{A_{12l}}(\eta'' - \eta^l)}{(v^l - v^v) + \frac{A_{2lv}}{A_{12l}}(v' - v^l) - \frac{A_{1lv}}{A_{12l}}(v'' - v^l)},$$

in which the exponents (′) and (″) refer to the phases $K_2Si_2O_5$ and $KHSi_2O_5$, respectively. The condition for a temperature maximum is that the denominator of this expression shall become zero; dp/dt become infinite. Since the volume difference between vapor and liquid is far greater than that between solid and liquid, the denominator will become zero only when the coefficients of the last two volume differences become very large, hence when the area of the triangle $K_2Si_2O_5$ - $KHSi_2O_5$ - L be comes very small. This point will be reached slightly before the liquid phase lies on the line $K_2Si_2O_5$ - $KHSi_2O_5$, hence the point of maximum temperature has been displaced slightly in the direction of the volatile component.

Summary.

In this paper the curves which represent the relation between the variations in pressure and temperature in monvariant systems, the P-T curves, are discussed on the basis of equations deduced by Gibbs. Theorems are developed showing under what conditions different P-T curves coincide, when the curves coincide throughout their course and when they are tangent, and whether they coincide in their stable or metastable portions. On the basis of the above theorems a method is developed for determining the order of successsion of the P-T curves which intersect at an invariant in a system of any number of components. This application is illustrated by applying it to the P-T curves proceeding from the quintuple points in the ternary system H_2O–K_2SiO_3–SiO_2. In addition, Gibbs' general equation for the slope of a P-T curve is discussed, and a method given for casting it into a form convenient for practical use. The application of this equation to the change in slope of a P-T curve with change in composition of a variable phase is illustrated by discussing various curves in the above-mentioned ternary system.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF OHIO STATE UNIVERSITY.]

A LEAD STANDARD CELL AND A DETERMINATION OF THE POTENTIAL OF THE LEAD ELECTRODE.

BY W. E. HENDERSON AND GEBHARD STEGEMAN.

Received November 11, 1917.

While engaged in a study of the transition temperature of some hydrated salts, a galvanic cell came under our observation which exhibited some interesting features, namely, its constancy of electromotive force and its reproducibility. An extended study was made of this cell, and the results appear in the following article.

The cell under consideration consisted in the following arrangement:

$$\text{Pb amalgam} — PbSO_4 — Na_2SO_4 10H_2O — Hg_2SO_4 — Hg$$

A study of lead amalgams has been made by Puschin,[1] and he has found that all amalgams having a percentage of lead between 1.8% and 66% exhibited the same electromotive force. Fay and North[2] state that an amalgam having a percentage of lead between the limits of about 2% and 55% is a two-phase system, consisting of a granular phase of constant composition (Pb_2Hg), and a liquid phase which also has a definite composition when equilibrium is reached. In the present investigation it has been found that amalgams having a percentage of lead between 2.5% and 6% possess a constant and reproducible electromotive force. Amalgams of higher concentration have not yet been studied by us. Such an amalgam should therefore serve well as one of the electrodes in a standard cell, and the results of this investigation appear to support this conclusion.

Preparation of Materials.

(*a*) **Lead Amalgams.**—The lead amalgams used were prepared by the electrolysis of a 10% solution of pure lead nitrate, using a mercury cathode and a platinum anode. A current of approximately 20 milliamperes was allowed to pass until the amalgam contained the desired percentage of lead, usually between 2.5% and 6% of lead.

(*b*) **Lead Sulfate.**—A dilute solution of sulfuric acid was slowly added to a dilute solution of lead nitrate and the precipitated sulfate repeatedly washed with distilled water. It was kept under water until ready to be used.

(*c*) **Sodium Sulfate.**—Three recrystallizations from distilled water were made to purify this salt. The crystals were kept in a moist condition to avoid efflorescence.

(*d*) **Mercurous Sulfate.**—The method described by Hulett[3] consisting in electrolyzing a solution of sulfuric acid (sp. gr. 1.15) with a mercury anode, was carefully followed. The gray product of this electrolysis was preserved in a dark-colored bottle under the acid used in its preparation.

(*e*) **Mercury.**—Ordinary mercury was stirred for two days in contact with dilute nitric acid and was then twice distilled under reduced pressure.

Preparation of the Cell.

The H type of cell was found to be very convenient and was made by joining two "culture tubes" together at a distance of about five cm. from

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[1] *Z. anorg. allgem. Chem.*, **36**, 201 (1903).

[2] *Am. Chem. J.*, **25**, 216 (1901).

[3] *Phys. Rev.*, **22**, 334 (1906).

the closed end. The amalgam was placed in one leg of the cell by means of a small bore pipet and mercury was introduced into the other leg in a similar manner. A paste composed of an intimate mixture of lead sulfate and sodium sulfate moistened with a solution saturated with both of these salts, was placed over the amalgam. Upon the mercury was placed a paste composed of an intimate mixture of lead sulfate, sodium sulfate and mercurous sulfate moistened by the previously mentioned solution. The sodium sulfate crystals comprised the largest part of the mixture. Both the lead sulfate and mercurous sulfate were washed free from acid (in a Gooch crucible) before being used in the cell in the manner employed by Hulett,[1] except that no alcohol was used. The washing material consisted of an aqueous solution saturated with both lead sulfate and sodium sulfate. An intimate mixture of lead sulfate and sodium sulfate was then used to fill up the cell to the cross arm, after which enough of the solution of lead sulfate and sodium sulfate was introduced to cover the crystals and fill the cross arm of the cell. Platinum wires sealed into small glass tubes extended down into both the amalgam and the mercury and served as a means of contact. Small cork stoppers, perforated to allow the passage of the wires, served to close the cell when it was placed in the thermostat. A little melted paraffin was then poured upon the stoppers, making them water-tight. The cells were kept at the desired temperature by placing them in a thermostat regulated to 0.01°.

A potentiometer reading directly to 0.00001 volt, in connection with a sensitive galvanometer, was used in making all measurements. A lead accumulator was employed as the source of current for the potentiometer and two certified Weston standard cells served as reference.

Two cells were prepared on December 12, 1916, and measurements of the voltages exhibited were made at frequent intervals to determine the constancy. The following table shows the readings obtained:

TABLE I.

Cell I. Amalgam 2.6% Pb.	Cell II. Amalgam 3.5% Pb.	Time of reading.	Temp.
0.96470	0.96453	Dec. 12, 1916	25°
0.96465	0.96470	Jan. 18, 1917	25°
0.96465	0.96465	Feb. 2, 1917	25°
0.96463	0.96464	March 2, 1917	25°
0.96463	0.96464	April 6, 1917	25°
0.96342	0.96343	April 15, 1917	18°
0.96342	0.96343	April 18, 1917	18°
0.96550	0.96552	April 19, 1917	30°
0.96550	0.96552	April 21, 1917	30°

To determine the reproducibility of this type of cell three new cells were prepared on February 12, 1917, and the voltages compared with those previously made.

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[1] Hulett, THIS JOURNAL, **38**, 23 (1916); cf. also *Phys. Rev.*, **22**, 234 (1906).

TABLE II.

Cell III.	Cell IV.	Cell V.	Time.	Temp.
0.96465	0.96461	0.96464	Feb. 12, 1917	25°
0.96465	0.96462	0.96463	Feb. 18, 1917	25°
0.96465	0.96462	0.96463	Mar. 12, 1917	25°
0.96464	0.96461	0.96462	Apr. 18, 1917	25°

This table shows that this cell is reproducible to within 3 hundredths of a millivolt, though a gradual decrease in voltage is noticeable over an extended range of time, a condition sometimes found in Weston and Clark cells. The electromotive force of this cell at any desired temperature may be found by means of the following equation, which has been verified by the values obtained at 18° and 30°, and shown in Table I:

$$E_t = 0.96463 + 0.000174\,(t - 25) + 0.00000038\,(t - 25)^2 \quad (1)$$

Calculation of the Heat Reaction.

In order to compare the heat of the reaction occurring in the cell, *viz.*,

$$0.5\ Pb_2Hg + Hg_2SO_4 \longrightarrow PbSO_4 + 2.5\ Hg,$$

with the available thermochemical data obtained at 18° by Thomsen, it is necessary to substitute the measured values of the cell in the Gibbs-Helmholtz equation:

$$Q = nF\left(E - T\frac{dE}{dT}\right)0.2387$$

At 18° the e. m. f. of the cell has been found to be 0.96343 volt, while the value of dE/dT, found by differentiating Equation 1, is +0.000169. The Gibbs-Helmholtz equation then assumes the form

$$Q = 2F\,(0.96343 - 291 \times 0.000169)\,0.2387 = 42{,}139 \text{ cals.}$$

Thomsen gives the heat of formation of lead sulfate as 216,200 cals. at 18°, while that of mercurous sulfate is given as 175,000 cals. The difference, 41,200 cals., then represents the free energy of the reaction

$$Pb + Hg_2SO_4 \longrightarrow PbSO_4 + 2Hg.$$

According to Luther,[1] an evolution of energy amounting to +585 cals. takes place when one gram-atom of lead is removed from the heterogeneous amalgam of which the solid phase is the compound Pb_2Hg. The true heat of reaction occurring in the cell, based upon thermochemical measurements, is therefore 41,200 + 585 or 41,785 cals.

Determination of the Potential of the Lead Electrode.

The constancy of the voltage of a lead amalgam such as was employed in the preparation of the cell described suggested that such an amalgam might be used in the determination of the potential of the lead electrode provided the difference in voltage between such an amalgam and a solid lead electrode were accurately known. A number of cells were accord-

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[1] *Z. Elektrochem.*, **17**, 293 (1911).

ingly prepared identical in every respect with those before described except that a solid lead electrode, made by precipitating lead electrolytically upon a heavy platinum wire from a 10% solution of lead nitrate, was substituted for the usual amalgam. Such electrodes were found to give a very constant voltage for at least two days, after which the voltage appeared to drop gradually. The fluctuation in voltage described by Getman[1] when lead precipitated upon platinum is placed in a solution of lead chloride was not apparent in these cells wherein the lead salt was the sulfate. The following table gives the voltage of four cells prepared in this manner:

Cell I.	Cell II.	Cell III.	Cell IV.	Temp.
0.96988	0.96965	0.96969	0.96972	25°

The difference between the mean value, 0.96973 and 0.96463, amounting to 0.0051 volt, is the difference in voltage existing between solid lead and the amalgam used in the cells.

The difference in potential existing between a 2 or 3% amalgam and a saturated solution of lead chloride which had been purified by two recrystallizations, was then measured against a battery of three electrodes constructed of the series 0.1 *N* $KCl-Hg_2Cl_2-Hg$. The calomel used in these electrodes was prepared by the electrolysis of a normal solution of hydrochloric acid with a mercury anode. The calomel was washed free from acid with a 0.1 *N* KCl solution before being used in the cell. The following values were obtained:

Amalgam I.	Amalgam II.	Amalgam III.	Amalgam IV.	Temp.
0.5138	0.5137	0.5135	0.5136	25°

There was no appreciable fluctuation in voltage during a two-day period so the mean of the values here given, 0.51367, is taken as the difference of potential existing between the amalgams used and an aqueous solution saturated with lead chloride. All of the amalgams were of different composition, ranging between 2% and 4% of lead. The resistance of the chain whose voltage was measured was so great that differences of 0.0001 volt were the smallest that could be accurately determined. Adding the value 0.0051 which is the difference between the amalgams used and a solid lead electrode we obtain 0.5187 volt as the potential of the chain

$$Pb — PbCl_2 \text{ sat.} — 0.1\ N\ KCl — Hg_2Cl_2 — Hg.$$

The Solubility of Lead Chloride and the Degree of Dissociation at This Dilution.

The solubility of lead chloride in water at 25° is given by D. M. Lichty[2] as 0.0388 mol per liter. The activity of the lead ion is given by Noyes and Toabe[3] at this dilution as 0.562 but is based, according to their state-

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[1] This Journal, 38, 792 (1916).

[2] *Ibid.*, 25, 469 (1903).

[3] *Ibid.*, 39, 1537 (1917).

ment, upon conductivity data and may therefore be subject to some error.

Since this work was done an article has appeared by Lewis and Brighton[1] in which they express the hope that in the near future they will be able to calculate the activity of the lead ion in a solution saturated with lead chloride. On the assumption that the activity of the lead ion in a saturated solution of lead chloride is 0.562% of the total concentration, the potential of the lead electrode is readily calculated by the equation

$$E = E^\circ - \frac{RT}{2F}\ln C$$

in which

$E = 0.5187$
E° = normal electrode potential
C = concentration in mols of the ion in question.

The equation then assumes the form

$$0.5187 = E^\circ - \frac{RT}{2F}\ln(0.0388 \times 0.562) \text{ or } E^\circ = 0.4696.$$

This is the value of the normal electrode of lead against the 0.1 *N* calomel electrode at 25°.

Summary.

A lead standard cell has been prepared which has been found to possess a constant voltage which is reproducible to within a few hundredths of a millivolt. It has been found that the voltage shows a gradual decrease over an extended range of time a property frequently found in other cells.

A determination of the potential of the lead electrode against the tenth normal calomel electrode has been made and found to be 0.4696 at 25°. This value may be subject to a change when the activity of the lead ion in the solution in question becomes more accurately known.

Columbus, Ohio.

[Contribution from the Wolcott Gibbs Memorial Laboratory of Harvard University.]

THE TRANSITION TEMPERATURES OF STRONTIUM CHLORIDE AND STRONTIUM BROMIDE AS FIXED POINTS IN THERMOMETRY.

By Theodore W. Richards and Victor Yngve.

Received October 29, 1917.

Introduction.

Some years ago one of us[2] pointed out that the transition temperatures of hydrated salts, since they are invariant points, serve excellently as

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[1] This Journal, 39, 1906 (1917).

[2] T. W. Richards, *Am. J. Sci.*, [4] 6, 201 (1898).