3. It was demonstrated by means of a comparison between the hydrogen-ion activities, obtained in the present investigation, and the values obtained with a hydrogen electrode, that the hydrogen electrode measures the hydrogen-ion activity and not the geometric mean of the activities of the hydrogen ion and the accompanying anion.

One of the authors of this paper (J. W. C.) wishes to express his thanks to the Department of Scientific and Industrial Research of the British Government, for a grant which enabled the research to be performed.

LIVERPOOL, ENGLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

TEMPERATURE COEFFICIENT OF ELECTROMOTIVE FORCE OF GALVANIC CELLS AND THE ENTROPY OF REACTIONS

BY ROSCOE H. GERKE

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The third law of thermodynamics in the limited form given by Lewis and Gibson[1] is becoming regarded as an exact law of nature. These authors have calculated the entropy of the elements and compounds,[2] for which heat-capacity data were available. They also tested the validity of the third law of thermodynamics by comparing the entropy change in a chemical reaction calculated on the one hand from heat-capacity data, and on the other hand from electromotive-force and thermochemical data. The discrepancies found amounted to over two entropy units on the average, but these were no greater than was to be expected, due to the inaccuracy of available calorimetric data.

The purpose of this investigation is to subject the third law of thermodynamics to a more rigorous test through more exact determination of entropy and heat content changes in a number of reactions. Such data can be determined with greater accuracy by a study of electromotive force of galvanic cells and its change with the temperature.

Experimental Considerations

By use of the equation $\frac{dE}{dT} = \frac{\Delta S}{nf}$, and by the Gibbs-Helmholtz equation, $\frac{\Delta H}{nf} = -E + T\left(\frac{dE}{dT}\right)$, the entropy change and the heat content change, respectively, may be calculated.

If the desired accuracy for the entropy change per equivalent is 0.10 calorie per degree, which corresponds to an accuracy of 30.0 calories for the change of heat content, the temperature coefficient of electromotive

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[1] Lewis and Gibson, THIS JOURNAL, **42,** 1533 (1920).

[2] Lewis and Gibson, *ibid.,* **39,** 2554 (1917).

force must be accurate to 0.000004 volt per degree. For 10.0° intervals the electromotive force of a cell at a given temperature must then be reproducible to 0.00004 volt, although it is not necessary for the cells to agree with each other better than to 0.0001 volt.

At a given temperature it is desirable to approach the equilibrium electromotive force from both lower and higher temperatures. This was quickly and conveniently done with a small hand-regulated thermostat, the temperature of which could be varied at will and regulated to 0.01°. As the electromotive force of the individual cells usually became constant to within 0.00001 volt in 30 to 60 minutes, a complete series of measurements could be made in a day. Cells must be free from vitiating factors, such as side reactions at the electrodes due to presence of dissolved oxygen, to the reaction of the electrode with the electrolyte, or to the cell reaction taking place at the electrodes themselves. Cells must also be free from liquid potentials. For example, the liquid potential[3] in the cell Pb, $PbCl_2$, HCl (1 *M*), AgCl, Ag, has been calculated to be 0.0020 volt, due to the absence of lead chloride at the silver—silver chloride electrode. If lead chloride is placed at the electrodes in both legs of the cell, it is obvious that there cannot be any liquid potential due to the lead chloride. The cell may now be written Pb, $PbCl_2$, HCl (1 *M*), $PbCl_2 + AgCl$, Ag. If the chemical substances be present at the electrodes as double salts, or contain water of crystallization, the entropy change would now correspond to a reaction like the following: $Pb + 2HgCl + KCl\ (x\ M) = KCl.PbCl_2 + 2Hg$. In this paper only simple salts are considered.

Furthermore, it is desirable that substances used in cells should be thermodynamically the same as those used in heat-capacity measurements, if comparisons between the two are to be made. For this reason chemically precipitated salts were employed instead of electrolytically precipitated salts. Also the electromotive behavior of metals depends upon the condition of the surface. It is thermodynamically necessary that two crystalline modifications of the same metal must have the same potential at the temperature of transition; at other temperatures the potentials may be measurably different. In addition, two samples of a pure metal of the same crystalline modification but of different past history, may exhibit slight differences of thermodynamic behavior due to strains. The softer the metal the less the magnitude of these effects.[4] The only surfaces free from strains are those of a pure liquid or of a liquid amalgam. Recent X-ray measurements[5] attest the truth of this statement. Distortion of the space lattice produced by rolling disappears almost instantly in case of lead and thallium, at room temperature, whereas

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[3] Ref. 2, p. 2577.

[4] Lewis and von Ende, THIS JOURNAL, **32**, 732 (1910).

[5] Nishikawa and Asahara, *Phys. Rev.*, **15**, 38 (1920).

in case of copper the recovery is observed in a few weeks. There is also a tendency to form surface films of insoluble salts on the surface of the electrode. If the surface be a liquid metal or an amalgam, the film is easily broken. Thus, there is always a clean electrode surface presented to the cell electrolyte. It is desirable to use 2-phase, saturated amalgams, since they are easily reproduced without analysis, and their reaction with the electrolyte does not change their composition. The cell may be designated as follows: Pb(Hg), $PbCl_2$, HCl(1 M), $PbCl_2$ + AgCl, Ag. The solid metal electrodes were compared with the amalgam electrodes in separate cells of the type, Pb, $Pb^{++}(x\ M)$, Pb(Hg). A cell solution containing the metal ion is chosen, which dissolves surface films and does not react with the electrodes. Both types of cells gave a constant and reproducible electromotive force, which rapidly responded to changes of temperature.

Apparatus

Potentiometer.—Measurements of electromotive force were made with a potentiometer of the decade-type box, which has been in use in this laboratory for several years. A complete description is given in a paper by Lewis, Brighton and Sebastian.[6] The potentiometer and all conductors connected therewith were thoroughly protected from stray electric effects by a conducting shield according to the method recommended by White.[7] By use of paraffined glass supports, all parts of the potentiometer system, including wires leading to cells and galvanometer, possessed a higher degree of insulation. A wire of 1 ohm resistance with a sliding contact was inserted in the working battery circuit in order that exact balance could be obtained between the working battery and the standard cell circuits.

Standard and Working Cells.—Standard cadmium cells were made from successive purifications of the cell materials, till the last two sets of cells agreed to 0.00001 volt. These were checked against each other and against fresh cells which were made up from time to time. They were immersed in an oil-bath at 25.00°.

As a working battery a large cell of the Hulett[8] type containing unsaturated cadmium sulfate solution proved extremely satisfactory.

Thermostats.—Oil thermostats were used, as water thermostats are not well adapted to precise measurements of electromotive force on account of electrical conductivity of films of moisture on glass apparatus. A complete description of the automatically controlled thermostat may be found in an article by Lewis, Brighton and Sebastian.[6] The small hand-

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[6] Lewis, Brighton and Sebastian, THIS JOURNAL, **39**, 2246 (1917).

[7] White, THIS JOURNAL, **36**, 2011 (1914).

[8] Hulett, *Phys. Rev.*, **27**, 33 (1908).

regulated thermostat[9] for measurements of electromotive force at various temperatures, consisted of an insulated cylindrical can of monel metal 20 cm. wide and 25 cm. deep. A copper cooling coil and a heating element of Chromel wire were wound round a copper sleeve 15 cm. wide and 20 cm. high which was centered in the can. A small motor-driven gear pump forced water at the rate of 1.5 liters per minute through the cooling coil. Efficient stirring was obtained by a propeller, the shaft of which extended through a stuffing gland in the bottom of the can. The oil circulated up and over the cooling and heating elements, between the sleeve and the walls of the can, and then down through the center of the sleeve, where the cells were suspended. The temperature could be changed a degree a minute and controlled to 0.01°.

Thermometer.—Temperatures were observed with a mercury thermometer,[10] which was compared with a Leeds and Northrup 25-ohm platinum resistance thermometer, the resistance of which was measured by comparing the potential drop across the thermometer with that of a standard 10-ohm resistance, when the two were connected in series. The potential drops were measured with a White double-combination potentiometer by Dr. F. Russell Bichowsky.

Materials

Elements.—Special attention was given to preparing the chemicals pure. For the silver electrodes, finely divided crystalline silver,[11] prepared by rapid electrolysis, was used. The stick lead electrodes were prepared by casting molten lead in a graphite mold. Electrical contact was made by thrusting a platinum wire, sealed in a glass tube, into the top of the stick of lead, where it was locally melted with the aid of a small blow torch. Sticks of thallium were made similar to those of lead. Chlorine was made by the electrolysis of fused lead chloride. In Fig. 1 is shown the electrolytic cell, which was constructed of Pyrex glass.

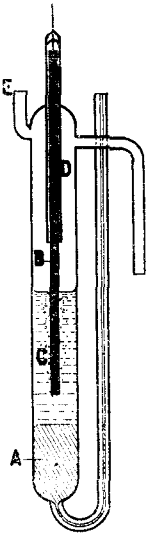

Fig. 1.—Chlorine generator.

The cathode (A) was molten lead, with which electrical contact was made by an iron wire through the capillary tube. The anode (B) of graphite dipped into the electrolyte (C) of fused lead chloride. A little potassium chloride was added to lower the melting point of the lead chloride. Electrical contact with the anode was made by screwing a threaded nickel wire into the graphite, and in turn the nickel wire was welded to a platinum wire, which was sealed through the Pyrex glass at the top of the generator. The glass tube (D) surrounding the graphite anode, served to keep it in position and also protected the nickel wire from corrosion by the chlorine. The mate-

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[9] Design suggested by Professor Merle Randall and built by Mr. G. F. Nelson.

[10] Baudin, No. 18047, thermometer was always immersed at the 0.00° mark and stem corrections were neglected as the room temperatures were quite uniform.

[11] Lewis, THIS JOURNAL, **28,** 158 (1906).

rials were introduced into the generator through the tube (E). A small electric furnace served to keep the apparatus at a temperature of about 450°.

This generator would operate continuously for weeks, yielding a slow, steady and easily controllable current of pure chlorine gas, which never came in contact with any substance, except glass. Cylinder nitrogen, the pressure of which was controllable by a reducing valve, was further purified from oxygen by bubbling through a series of five 40cm. columns, which were filled with copper wire and ammoniacal ammonium carbonate solution. To remove the ammonia gas, a wash bottle was inserted which contained dil. sulfuric acid. It was not necessary to remove water vapor. Next the nitrogen gas and water vapor were led to a 3-way stopcock, which either connected the gas stream to the flask containing cell electrolyte to be saturated with the inert gas or diverted the gas to the atmosphere, while the flask was being evacuated.

Amalgams.—A 2-phase amalgam, containing about 5% of lead, consisting of the compound Pb_2Hg[12] and liquid solution was made by dissolving lead in hot mercury. A 40% thallium amalgam, consisting of 2 phases,[13] was made by electrolyzing thallous sulfate solution and using a mercury cathode.

Solid Salts.—The halides of lead, silver, thallium and mercury[14,15] were precipitated metathetically in the ordinary granular form from dilute solutions of pure salts containing the necessary ions. Before placing them in cells, it was the custom to wash by decantation at least 6 times with solution used as the cell electrolyte. It may be mentioned that thallous chloride was recrystallized once from doubly distilled water. The

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[12] Fay and North, *Am. Chem. J.*, **25,** 216 (1901).

[13] Jones and Schumb, *Proc. Am. Acad. Arts Sci.*, **56,** 212 (1919). Richards and Daniels, THIS JOURNAL, **41,** 1765 (1919).

[14] Ref. 6, p. 2251.

[15] Since the potential of the calomel electrode depends somewhat on the method of preparation, it may be well to restate the conditions under which it acts as a reversible electrode in molal potassium chloride. Chemically precipitated calomel was made by the addition of dil. hydrochloric acid to dil. mercurous nitrate in nitric acid solution in equilibrium with mercury. The mercurous chloride was washed by decanting at least 6 times with *M* potassium chloride solution and was shaken with mercury to insure the following equilibrium: $Hg_2^{++} + 2\ Cl^- = Hg + HgCl_2$. Such calomel, whether or not washed with *M* potassium chloride solution after shaking with mercury, gives within 0.0002 volt the same potential as calomel prepared by electrolysis of hydrochloric acid using a mercury anode, while calomel which has not been equilibrated with mercury may differ from the equilibrated variety as much as 0.001 volt.

It was observed that calomel in potassium chloride solutions on long standing is alkaline to phenolphthalein. This development of alkalinity may be ascribed to slow oxidation of the mercury by atmospheric oxygen, according to the following reaction: $2Hg + {}^1/_2O_2 + 2Cl^- + H_2O = Hg_2Cl_2 + 2OH^-$, which involves the removal of chloride ion in dilute solutions of potassium chloride and thus causes discrepancies in the potential of the calomel electrode.

photosensitive halides of silver and of thallium were protected from the direct action of bright sunlight; otherwise no precaution of such character seemed necessary, since the oil in the thermostat was sufficiently dark.

The Galvanic Cells

Glass parts.[16]—The H type of cell, Fig. 2, was ordinarily used because of its simplicity and low internal resistance, which makes for high sensitivity of the galvanometer. Electrical contact at the electrodes was made by platinum wires sealed in the glass. A little bulb (a) at the base of the electrode containing liquid mercury or amalgam, prevented the cell electrolyte from coming into contact with the platinum wire.

For cells involving stick metal and amalgam, simple half cells were employed in which the metal was supported above the amalgam. For the combination, Tl (sticks), TlOH, Tl (Hg), a platinum test-tube[17] was used, which was supported in one of the half cells.

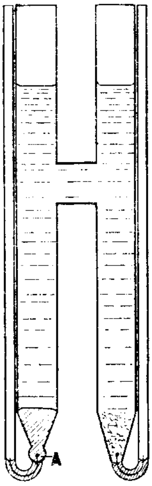

Fig. 2.—H-cell.

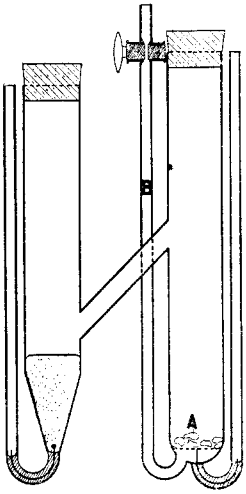

Fig. 3.—N-cell.

The N type of cell used for the reaction, Pb (crystal) = Pb (Hg), had a platinum basket upon which the crystals of lead were electrically precipitated with low current density. The basket (A), Fig. 3, also served as a support for the lead crystals. The glass tube (B) which enters the cell just beneath the platinum basket makes possible circulation of the cell electrolyte, so that difference in concentration produced by the electrolysis may be removed.

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[16] The glass apparatus was constructed by Mr. Wm. J. Cummings.

[17] A Lawrence Smith crucible. Platinum was necessary, as it is one of the few substances conducting electricity that are less electropositive than thallium but do not form a liquid alloy with mercury at ordinary temperatures and do not react with thallous hydroxide. With glass, thallous hydroxide forms thallous silicate.

In the H-cell involving solid iodine, either dip electrodes of a platinum spiral or of a 15% iridium plate served to make electrical connection with the saturated iodine solution instead of the customary platinum wire sealed in the bottom of the leg of the cell.

The chlorine—silver-chloride—silver cell is shown in Fig. 4. In the main, it is of the same design as used by Lewis and Rupert.[18] The cell was constructed of Pyrex glass, so that it could be sealed directly to the chlorine generator, without the aid of greased ground-glass joints or de Khotinsky seals, which are attacked by the chlorine. The chlorine electrode is of 15% iridium platinum alloy. The new feature consisted in a countercurrent periodic flow of hydrochloric acid through the cell, to prevent the chlorine from reacting with the silver. The separatory funnel served as a source of the hydrochloric acid, which filtered through the silver-silver chloride electrode (B). The waste liquors were caught by the trap (C). It was found that the diffusion of the chlorine from the chlorine electrode to the silver-silver chloride electrode was largely prevented by a small plug of glass wool covered with a deep layer of precipitated silver chloride, which was situated at the bend (D). The cork through which passed the support of the platinum basket was coated with paraffin, to prevent the evaporation of water from the solution in the region of the silver-silver chloride electrode.

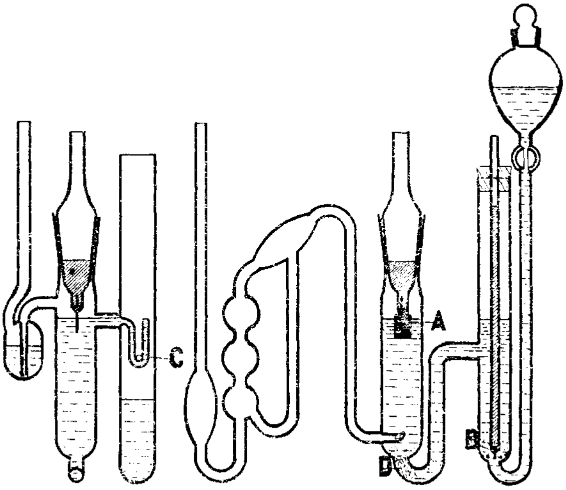

Fig. 4.—Chlorine cell.

Filling of Cells.—With the exception of the combination, Ag, AgCl, HCl (1 *M*) or KCl (1 *M*), HgCl, Hg, all cell electrolytes were free from dissolved oxygen, which was removed by evacuation and replaced by nitrogen. This somewhat complicated the procedure which

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[18] Lewis and Rupert, THIS JOURNAL, **33**, 299 (1911).

is ordinarily very simple. As an illustration, the details of filling the cell, Tl (Hg), TlCl, NaCl (1 *M*), HCl (0.001 *M*) + TlCl + AgCl, Ag, in which the following reaction tends to take place, Tl (Hg) + AgCl = TlCl + Ag, will be described. Finely divided silver[19] which had been dried in an oven at 100° was poured into one leg of the cell, which was gently tapped in order to make the silver pack slightly and effect contact with the platinum wire in the bottom of the cell. The air was displaced from the cell by passing a current of nitrogen through the cell for a few minutes; with the stream of nitrogen still flowing to prevent entrance of air, hot liquid thallium amalgam, (80° or 90°) was transferred into the other leg of the cell by means of a previously warmed pipet. On cooling, the solid phase separated. The surface was always bright and free from oxide. Silver and thallous chlorides[20] suspended in the cell electrolyte, which had been evacuated and saturated with nitrogen, were pipetted onto the silver. To complete the cell, enough oxygen-free cell electrolyte with thallous chloride in suspension was run in to fill the bar of the "H." This was done by forcing the liquid from the wash bottle[21] into the cell by means of nitrogen under pressure, taking no precaution to prevent thallous chloride from settling in either leg of the cell. The only necessary precaution was that the transfer was made carefully enough to prevent the convection of silver chloride to the thallium amalgam electrode, which was further protected from the presence of traces of silver chloride by a layer of solid thallous chloride about 1 cm. deep. The cell was sealed with corks saturated with hot beeswax and rosin mixture.

Immediately after making, the cells were transferred to the constant-temperature thermostat at 25°. Usually in less than 24 hours the electromotive force became constant to a few hundredths of a millivolt, when two or three cells were transferred to the variable temperature thermostat. They were supported by rods and clamps, which were sufficiently independent of the thermostat to be free from vibrations. Vigorous shaking would often change the electromotive force by as much as 0.0002 volt. Usually, however, on standing for a few minutes the electromotive force would return to its former value within 0.00001 volt.

After the electromotive force had become constant, for example at 25.00°, the temperature would be changed perhaps to 35.00°, then to 45.00°,

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[19] In cells in which dissolved oxygen was of no consequence the finely divided silver immersed in the cell electrolyte was transferred to the cell by means of a glass hook.

[20] It was later found to be unnecessary to evacuate the AgCl suspensions, when all the supernatant liquid was removed with a pipet after making the transfer to the cell. A little dissolved oxygen at the silver electrode does not interfere with the operation of the Tl (Hg) electrode.

[21] The Pyrex wash bottle of 1 liter capacity was attached to the nitrogen line in such a way that by the manipulation of a 3-way stopcock the bottle could be open to the vacuum line (0.1 mm. pressure) or to the nitrogen supply.

50.00°, 45.00°, 35.00°, 25.00°, etc. A series of such measurements, in which each temperature was approached from both above and below, constituted a run. It was attempted to remove the element of prejudice on the part of the observer. In many cases galvanometer readings were made by different observers[22], when the temperature was approached from above and from below.

Experimental Values of Electromotive Force of the Various Cells at Different Temperatures

THE CELL AG, AgCl,HCl (1 *M*) + AgCl, Cl_2 (1 ATM.).—Of the numerous investigations of the potential of the chlorine electrode, only one[23] gives temperature coefficients of electromotive force. It has been pointed out[24] that in order to obtain the potential of chlorine, free from errors due to the solubility of the chlorine, the hydrolysis of chlorine and the formation of the trichloride ion, it is advisable to use dil. chlorine gas. It is difficult to construct cells involving dil. chlorine that have the necessary reproducibility or constancy of electromotive force for entropy calculations. Therefore, it was hoped that the cell, Ag, AgCl, HCl (1 *M*), AgCl, Cl_2 (1 atm.), with the silver chloride at both electrodes would give an electromotive force that could be measured with precision. The only errors due to reaction of the chlorine with the chemical substances in the cell are the formation of trichloride ion or a complex ion with silver chloride, since the hydrolysis of chlorine is negligible in molal hydrochloric acid. If these reactions take place to the same degree at different temperatures,

TABLE I
THE CELL Ag, AgCl, HCl (1 *M*) + AgCl, Cl_2 (1 ATM.)

Date	Temp. °C.	Bar. pres. Mm.	Pres. of Cl_2 Mm.	E.m.f. obs. Volts	E.m.f. cor. Volts	E.m.f. Cl_2 1 atm. Volts	Temp. coef.
11/15/21	34.96	754.7	712.5	0.11142	0.00085	1.13037	
							−0.000605
11/17/21	24.86	755.8	732.0	0.11790	0.00048	1.13648	
							−0.000594
11/19/21	34.96	759.8	717.6	0.11163	0.00077	1.13050	
							−0.000597
11/21/21	24.86	753.6	729.8	0.11793	0.00051	1.13654	
12/5/21	24.86	755.7	731.9	0.11757	0.00048	1.13615	
							−0.000580
12/8/21	14.90	761.1	748.3	0.12359	0.00020	1.14189	
							−0.000598
12/9/21	24.86	760.5	736.7	0.11747	0.00039	1.13596	
						Mean	−0.000595

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[22] The writer wishes to acknowledge the assistance of Mr. Roy Bauer and Mr. John Shell in making some of the runs.

[23] Wolff, *Z. Elektrochem.*, **20,** 19 (1914).

[24] Ref. 18, p. 306.

the entropy of the reaction could be calculated from the temperature coefficient of electromotive force of the cell. All the measurements are exhibited, from which the temperature coefficient may be calculated. The formation of the solid hydrate at 5° and the evaporation of the water of the cell electrolyte at 35° restricted accurate measurements of electromotive force of this cell to the 15–25° range. However, the temperature coefficients for the 35–25° range are more apt to be correct than are those of the 25–35° range.

THE CELL Hg, HgCl, HCl (1 *M*), Cl_2 (1 ATM.)[25].—Mere repetition of the measurements of the previous cell would constitute a less valuable check than would measurements on this cell. Moreover, the cell electrolyte, hydrochloric acid, in the latter cell was not saturated with silver chloride as in the former. The principal change in the filling of the cell was the use of standard sand washed with alkali, acid, and bromine dissolved in acid, in place of silver chloride to prevent diffusion of the chlorine to the calomel electrode.

TABLE II

THE CELL Hg, HgCl, HCl (1 *M*), Cl_2 (1 ATM.)

Date	Temp. °C.	Bar. pres. Mm.	Pres. of Cl_2 Mm.	E.m.f. obs. Volts	E.m.f. cor. Volts	E.m.f. Cl_2 1 atm. Volts	Temp. coef.
3/26/22	24.88	756.0	732.2	0.07181	0.00045	1.09036	
							−0.000949
3/28/22	15.05	755.1	742.3	0.08127	0.00031	1.09968	
							−0.000945
3/29/22	24.86	756.1	732.4	0.07187	0.00044	1.09041	
							−0.000900
3/30/22	34.96[a]	756.2	714.0	0.06240	0.00083	1.08133	
							−0.000944
3/31/22	24.86	752.5	728.7	0.07223	0.00054	1.09087	
4/1/22[b]	24.86	753.9	730.1	0.07177	0.00051	1.09038	
							−0.000940
4/2/22	15.03	752.3	739.5	0.08119	0.00033	1.09962	
							−0.000947
4/3/22	24.88	752.3	729.5	0.07166	0.00053	1.09029	
						Mean	−0.000945

[a] It will be observed that the 35° and the subsequent 25° value for the electromotive force is high, which invalidates the temperature coefficient for the 25–35° range, while the 35–25° value agrees well with the others.

[b] At this time 200 to 250 cc. of 1 *M* HCl was passed through the cell, whereupon the electromotive force again becomes normal.

In Table III are the values for the cell Ag, AgCl, KCl (1 *M*), HgCl, Hg. Brönsted,[26] using electrolytic silver chloride electrodes after the method

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[25] Ref. 23. The best value given by this author for the electromotive force of this cell at 25° is 1.0843 volts and the temperature coefficient of electromotive force is —0.00100 volts per degree.

[26] Brönsted, *Z. physik. Chem.*, **50**, 581 (1904).

of Jahn,[27] obtains for the combination, Ag, AgCl, KCl (gel), HgCl, Hg, at the following temperatures the corresponding electromotive forces: 15.0°, 0.0439; 32.0°, 0.0498; 44.0°, 0.0554; 58.5°, 0.0596; 73.3°, 0.0652; 88.0°, 0.0708, which give the following temperature coefficients of e.m.f.; 0.000347, 0.000350, 0.000386, 0.000381, 0.000387.

TABLE III

THE CELL Ag, AgCl, KCl (1 *M*), HgCl, Hg

Temp. °C.	E.m.f. I Volts	$\Delta E/\Delta T$	E.m.f. II Volts	$\Delta E/\Delta T$	E.m.f. III Volts	$\Delta E/\Delta T$
24.86	0.04551		0.04552		0.04545	
		0.000336		0.000337		0.000340
14.86	0.04215		0.04215		0.04205	
		0.000336		0.000335		0.000336
5.00	0.03879		0.03880		0.03869	
		0.000334		0.000335		0.000331
14.86	0.04213		0.04215		0.04200	
		0.000339		0.000337		0.000344
24.86	0.04552		0.04552		0.04544	
		0.000339		0.000339		0.000340
34.96	0.04894		0.04894		0.04887	
40.00	0.05065		0.05064		0.05059	
34.96	0.04893		0.04893		0.04888	
	Mean	0.000337		0.000337		0.000338

In Table IV are the values for the cell Ag, AgCl, HCl (1 *M*), HgCl, Hg.

TABLE IV

THE CELL Ag, AgCl, HCl (1 *M*), HgCl, Hg

Temp. °C.	E.m.f. I Volts	$\Delta E/\Delta T$	E.m.f. II Volts	$\Delta E/\Delta T$	E.m.f. III Volts	$\Delta E/\Delta T$
24.86	0.04536		0.04544		0.04548	
		0.000337		0.000338		0.000337
14.86	0.04199		0.04206		0.04211	
		0.000334		0.000335		0.000334
5.00[a]	0.03865		0.03871		0.03877	
		0.000334		0.000337		0.000335
14.86	0.04199		0.04208		0.04212	
		0.000340		0.000339		0.000338
24.86	0.04529		0.04547		0.04550	
		0.000338		0.000337		0.000337
34.96	0.04880		0.04887		0.04890	
34.96	0.04880		0.04886		0.04890	
		0.000339		0.0003395		0.000338
24.86	0.04537		0.04543		0.04548	
	Mean	0.000336		0.000338		0.000337

[a] Since the 5.0° point on the thermometer had not been calibrated, the 15–25° and 25–35° intervals should be given the most weight.

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[27] Jahn, *Z. physik. Chem.*, **33**, 545 (1900).

THE CELL Pb, Pb^{++}, Pb (Hg).—Many measurements of the potential of lead electrode[28] have been made, but hitherto no one has accurately measured the temperature coefficient of a cell involving a solid lead electrode. Since the measurements in this paper were made, it is noted that Krahmer[29] has published results which are irreconcilable with those in this paper. However, he states that the e.m.f. of his cells was a function of their age, which he attributed in part to the size of the metal granules on the surface of the lead. The conclusion of Lewis and Brighton that their experiments furnished no evidence for the allotropic change of lead as described by Getman[30] has been confirmed by the measurements in this paper. Much additional evidence[31,32] has been adduced, which indicates that such transformations are due to impurities between the grains of lead.

Dissolved oxygen was not present in the cell electrolyte. The following runs are for individual cells, which on the average gave steady e.m.f.'s in 2 hours.

TABLE V

THE CELL, Pb (ELECTROLYZED CRYSTALS), $PbAc_2$ (1 M), Pb(Hg)

Date	Temp. °C.	E.m.f. Volts	$\Delta E/\Delta N$	E.m.f. Volts		$\Delta E/\Delta T$
9/11/20	25.0	0.00585				
			0.000012			
	30.0	0.00591		0.00591		
			−0.000002			0.000016
	35.0	0.00590		0.00599		
			0.000006			0.000014
	40.00	0.00593		0.00606		
			0.000010			−0.000014
	45.00	0.00598		0.00599		
					Mean[a]	
9/13/20	25.00	0.00587		0.00585		
			0.000016			0.000014
	15.00	0.00571		0.00572		
			0.000010			0.000013
	5.00	0.00561		0.00558		
					Mean	0.000013
9/14/20	15.00	0.00553				
			0.000023			
	5.00	0.00530				
	5.00	0.00531				
			0.000020			
	15.00	0.00551				

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[28] See Lewis and Brighton, THIS JOURNAL, **39**, 1906 (1917), for references.

[29] Krahmer, *Z. Elektrochem.*, **26**, 97 (1920).

[30] Getman, THIS JOURNAL, **38**, 792 (1916).

[31] Rawdon, *Bur. Standards Sci. Papers*, **377** (1920).

[32] Thiel, *Ber.*, **53**, 1052 (1920).

TABLE V (continued)

Date	Temp. °C.	E.m.f. Volts	$\Delta E/\Delta T$	E.m.f. Volts	$\Delta E/\Delta T$
			0.000021		
9/14/20	25.00	0.00572			
			0.000019		
	35.00	0.00591			
			0.000005		
	45.00	0.00596			
	45.0	0.00597			
			0.000006		
	35.0	0.00591			
			0.000016		
	25.0	0.00575			
			0.000016		
	35.0	0.00591			
			0.000005		
	45.0	0.00596			
		Mean	0.000021[b]		

[a] No mean value was taken because of fluctuations in the temperature coefficient.

[b] Weighted mean, with 35–45° values for $\Delta E/\Delta T$ omitted.

In Table VI are the values for the cell, Pb (stick), $Pb(Ac)_2$, Pb(Hg).

TABLE VI

THE CELL, Pb (STICK), $Pb(Ac)_2$, Pb(Hg)

Date	Temp. °C.	E.m.f. Volts	$\Delta E/\Delta T$	E.m.f. Volts	$\Delta E/\Delta T$
9/8/20	20.00	0.00556			
			0.000012		
	30.00	0.00568		0.00575	
			0.000017		0.000014
	40.00	0.00585		0.00589	
			0.000016		0.000012
	50.00	0.00601		0.00601	
				Mean	0.000014
9/11/20	25.00	0.00567			
			0.000016		
	30.00	0.00575		0.00579	
			0.000016		0.000016
	35.00	0.00583		0.00586	
			0.000014		0.000014
	40.00	0.00590		0.00593	
			0.000014		0.000014
	45.00	0.00597		0.00600	
				Mean	0.000015

In Table VII are the values for the cell, Pb (stick), $Pb(ClO_4)_2$, Pb(Hg). Some dissolved oxygen was present in the cell electrolyte. In the temperature-coefficient runs the cells gave steady electromotive force.

Table VII

The Cell, Pb (Stick), $Pb(ClO_4)_2$, Pb(Hg)

Date	Temp. °C.	E.m.f. Volts	$\Delta E/\Delta T$	Date	Temp. °C.	E.m.f. Volts	$\Delta E/\Delta T$
7/24/20	45.00	0.00567		7/26/20	25.00	0.00566	
			0.000018				
	35.00	0.00585		7/27/20	25.00	0.00567	
							0.000019
7/25/20	24.00	0.00573			35.00	0.00586	
			0.000018				
	35.00	0.00586		7/28/20	45.00	0.00604	
			0.000021				
	45.00	0.00607					

For the cell, Pb (solid), Pb^{++}, Pb (Hg), Pb (solid), is an average of three means; fresh electrolyzed crystals, old electrolyzed crystals and stick lead. In all cases the cell electrolyte was oxygen-free. The final value is $E_{298} = 0.0057$; $\Delta E/\Delta T = 0.000016$.

In Table VIII are the values for the cell, Pb (Hg), $PbCl_2$, HCl (1 M), $PbCl_2$, AgCl, Ag. Data for only 1 of 2 cells made are given, as 1 gave very discordant temperature coefficients, due to accidental presence of silver chloride at the lead amalgam electrode.

Table VIII

The Cell, Pb (Hg), $PbCl_2$, HCl (1 M) + $PbCl_2$, AgCl, Ag

Date	Temp. °C.	E.m.f. Volts	$\Delta E/\Delta T$	Date	Temp. °C.	E.m.f. Volts	$\Delta E/\Delta T$
10/22/20	24.86	0.484315		10/24/20	24.86	0.484340	
			−0.000200				−0.000203
	34.96	0.482280			14.86	0.486370	
			−0.0002005				−0.000200
	45.05	0.480247			5.00	0.488370	
							−0.000196
	45.05	0.480253			14.86	0.486410	
			−0.000206				−0.000205
	34.96	0.482335			24.86	0.484365	
			−0.000202				−0.000202
	24.86	0.484375			34.96	0.482310	
							−0.000204
10/23/20	24.86	0.484365			45.05	0.480252	
			−0.000200				
	14.86	0.486365			45.05	0.480280	
			−0.000200				−0.000205
	5.00	0.488370			34.96	0.482367	
		Mean	−0.000202			Mean	−0.000202

In Table IX are the values for the cell, Pb (Hg), $PbCl_2$, HCl (1 M), $PbCl_2$, HgCl, Hg.[33] Although the data for these cells are not so concor-

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[33] Babinski, *Dissertation,* Leipzig, **1906,** obtains for a similar combination, as an average of his results, $E = 0.5304 + (t - 30)\ 0.00013$.

dant, they will be exhibited as a check on the previous combination, involving the halides of silver and of lead.

Table IX

The Cell, Pb (Hg), $PbCl_2$, HCl (1 *M*), $PbCl_2$ + HgCl, Hg

Date	Temp. °C.	E.m.f. I Volts	$\Delta E/\Delta T$	E.m.f. II Volts	$\Delta E/\Delta T$
10/14/20	25.0	0.53001		0.52991	
			0.000121		0.000132
	35.0	0.53121		0.53123	
			0.000133		0.000129
	25.0	0.52988		0.52994	
10/15/21	25.0	0.52989		0.52993	
			0.000131		0.000131
	34.96	0.53120		0.53124	
			0.000136		0.000133
	45.0	0.53256		0.53257	
10/16/20	45.2	0.53257		0.53260	
			0.000131		0.000133
	35.0	0.53126		0.53127	
			0.000147		0.000148
	24.79	0.52979		0.52979	
	24.98	0.52974		0.52979	
			0.000123		0.000115
10/17/20	15.0	0.52851		0.52864	
			0.000100		0.000106
	5.0	0.52751		0.52758	
	5.0	0.52744		0.52749	
			0.000112		0.000109
	15.0	0.52856		0.52858	
			0.000131		0.000131
	25.0	0.52987		0.52989	
		$E_{298} = 0.5299$			
		Mean	0.0001261		0.0001252
	Weighted mean		0.0001305[a]		0.0001281
	Average of weighted means		0.000129		

[a] Weighted mean excludes only the first 25° value, and the two 15–5° values.

In Table X are the values for the cell Tl(Stick), TlOH, Tl(Hg). Richards and Daniels[34] find $E_{20°} = 0.0025$, and $\Delta E/\Delta T$ (0–20°) = 0.0000142, and $\Delta E/\Delta T$ (20–30°) = 0.0000179, or an average for $\Delta E/\Delta T$ of 0.000016. Jones and Schumb[35] find $E_{25°} = 0.0028$, $E_{0°} = 0.0018$, and $\Delta E/\Delta T = 0.00004$.

A value for $\Delta E/\Delta T$ will be calculated from data of Richards and Daniels, and of Lewis and Randall.[36]

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[34] Richards and Daniels, This Journal, **41,** 1740 (1919).

[35] Jones and Schumb, *Proc. Am. Acad. Arts Sci.*, **56,** 217 (1919).

[36] Lewis and Randall, This Journal, **43,** 233 (1921).

(I) Tl(s) = Tl(n_2 = 0.336); T = 30°; E = 0.01246; ΔF = —289 cal. $\Delta H = L_2$ (Tl, n_2=0.336) $-L_2$ (Tl, n_2=1) = 1457 − 730 = + 720 cal. From the equation, $\Delta S = (-\Delta F + \Delta H)/T$, ΔS = + 3.34 cal./deg. and $\Delta E/\Delta T$ = +0.000145.

(II) Tl (n_2=0.336) = Tl (Hg, 2-phase); T=30°; $\Delta E/\Delta T$ = —0.000126 volt. /deg.

If I and II are added, the equation, Tl(s) = Tl (Hg, 2-phase), is obtained for which the temperature coefficient of electromotive force, $\Delta E/\Delta T$, is calculated to be +0.000019 volt/deg. Richards and Smyth[37] give the value for the potential of the cell Tl (solid casting), Tl_2SO_4, Tl(Hg), at 20° as 0.0021 volt, whereas the cell Tl (crystals by electrolysis), Tl_2SO_4, Tl(Hg), at 20° is given as 0.0027. They state, however, that the high value for the electrolytic crystals approaches that of the cast sticks after long standing.

TABLE X

THE CELL, Tl (STICK), TlOH, Tl (Hg)[a]

Date	Temp. °C.	E.m.f. Volts	$\Delta E/\Delta T$	Date	Temp. °C.	E.m.f. Volts	$\Delta E/\Delta T$
5/3/21	Cell made			5/9/21	25.00	0.00238	
5/4/21	25.00	0.00273					
			0.000021				0.000028
	45.00	0.00315			35.00	0.00266	
			0.000018				0.000029
	25.00	0.00279			45.00	0.00295	
		Mean	0.000020				0.000022
5/5/21	25.00	0.00271			50.00	0.00306	
			0.000025				0.000018
	35.00	0.00296			45.00	0.00297	
			0.000023				0.000035
	45.00	0.00319			35.00	0.00262	
			0.000017				0.000021
	35.00	0.00302			25.00	0.00241	
			0.000029			Mean	0.0000261
	25.00	0.00273		5/30/21	20.00	0.00213	
		Mean	0.0000235				0.000038
					30.00	0.00251	
							0.000034
					35.00	0.00268	
							0.000028
					30.00	0.00254	
							0.000032
					35.00	0.00270	
							0.000032
					40.00	0.00286	
							0.000026
					30.00	0.00260	
							0.000036
					20.00	0.00224	
						Mean	0.000032

[a] Tl(OH) (1 M approx.) was used to get high concentration of Tl^+ and because H^+ in TlOH does not tend to oxidize the thallium.

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[37] Richards and Smyth, THIS JOURNAL, **44**, 524 (1922).

In the experiment of May 9, a deposit of crystalline thallium near the surface of the thallous hydroxide solution was found to have grown on the platinum wire which supported the thallium stick. This accounts for the decrease in electromotive force and for the increase of the temperature coefficient of electromotive force, since the free energy and entropy of any supercooled liquid thallium between the crystals would decrease and increase, respectively, when transformed into the crystalline modification.

In Table XI are values for the cell Tl (Hg), TlCl, NaCl (1 *M*) + HCl (0.001 *M*), TlCl + AgCl, Ag. The measurements are given only for the temperature range 25.0° to 45.0°, as the cells did not give a reproducible e.m.f. below 25° since the thallium amalgam existed only as solid phase at about 20°. However, the temperature could be lowered to 15°, and when raised to 25°, the potential was identical with that before cooling.

Lewis and Von Ende[4] have studied the potential of the thallium electrode; more recently Jones and Schumb,[13] have made measurements using thallium electrodes; the latter have measured the temperature coefficients.

TABLE XI

THE CELL, Tl (Hg), TlCl, NaCl (1 *M*) + HCl (0.001 *M*), TlCl + AgCl, Ag

Temp. °C.	E.m.f. I Volts	$\Delta E/\Delta T$	E.m.f. II Volts	$\Delta E/\Delta T$
34.98	0.77579		0.77577	
		0.000081		0.000081
45.05	0.77497		0.77495	
45.05	0.77498		0.77496	
		0.000081		0.000081
34.96	0.77580		0.77578	
		0.000078		0.000077
24.86	0.77659		0.77656	
		0.000079		0.000079
34.96	0.77579		0.77576	
			Mean	0.000080
30.00	0.77617		0.77613	
		0.000080		0.000078
40.00	0.77537		0.77535	
40.00	0.77539		0.77535	
		0.000079		0.000080
30.00	0.77618		0.77615	
	Mean		Mean	0.0000795

In Table XII are the values for the cell Pb (Hg), PbI_2, $Pb(ClO_4)_2$ (0.218 *M*) + $HClO_4$, PbI_2, I_2. Hitherto, numerous investigations of the potential of the iodine electrode have been made which involve uncertain corrections, such as liquid potentials purposely inserted and also the one caused by the formation of tri-iodide ion. Since no direct comparisons of measurements can be made, it may be well not to insert them at this point.

It may not be apparent at a first glance that this combination gives a potential, that corresponds to the reaction, Pb (Hg) + I_2 = PbI_2. If the separate electrode reactions are written it becomes obvious at once that any corrections due to liquid potential and to tri-iodide ion formation have been eliminated by using a lead salt as the cell electrolyte, thus making the cell reversible to lead ion instead of iodide ion. A calculation shows that the magnitude of these corrections is less than the experimental error. If lead iodide should be precipitated from a solution of lead ion saturated with iodine it would not be possible to use a solution containing lead ion for the cell electrolyte.

Table XII

The Cell, Pb (Hg), PbI_2, $Pb(ClO_4)_2$ (0.218 *M*) + $HClO_4$, PbI_2, I_2

Temp. °C.	E.m.f. I Volts	$\Delta E/\Delta T$	E.m.f. II Volts	$\Delta E/\Delta T$
24.86	0.89362		0.89362	
		−0.000044		−0.000044
34.96	0.89318		0.89318	
		−0.000044		−0.000044
45.05	0.89274		0.89274	
45.05	0.89274		0.89273	
		−0.000047		−0.000047
34.96	0.89321		0.89320	
24.86	0.89363		0.89362	
		−0.000041		−0.000040
14.86	0.89404		0.89402	
		−0.000038		−0.000038
5.0	0.89442		0.89440	
		−0.000039		−0.000037
14.86	0.89403		0.89403	
	Mean	−0.000042	Mean	−0.000042

In Table XIII are the values for the cell Pb (Hg), PbI_2, KI (1 *M*), PbI_2 + AgI, Ag. Taylor,[38] using electrolytic silver iodide finds for the combination (I), Pb (Hg) (0.72 *M*), PbI_2, KI, AgI, Ag, and using for (II) Pb (solid) = Pb (Hg) (0.72 *M*), Brönsted's value E_{11} = 0.0051 + 0.000233 *t*, the combination, (III), Pb (solid), PbI_2, KI, AgI, Ag, may be calculated.

KI	$E_{(I)0°}$	$E_{(I)25°}$	$\Delta E/\Delta T_{(I)}$	$\Delta E/\Delta T_{(III)}$
0.05	0.20965	0.20065	−0.000360	−0.000127
0.10	0.20905	0.19977	−0.000372	−0.000139

More recently Taylor and Perrott[39] exhibit measurements on the following cells; Cd (Hg), $CdCl_2.2H_2O$, PbI_2, Pb (Hg) (0.72) and Cd (Hg), $CdCl_2.2H_2O$, AgI, Ag, from which cell (I) above may be calculated. They

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[38] Taylor, This Journal, **38**, 2295 (1916).

[39] Taylor and Perrott, *ibid.*, **43**, 489 (1921).

mention, however, difficulties in obtaining at once reproducible results with the silver iodide cell, due to the possible formation of a cadmium-silver complex.

$E_{(I)0°}$	$E_{(I)25°}$	$\Delta E/\Delta T_{(I)}$	$\Delta E/\Delta T_{(III)}$
0.20405	0.19625	0.000312	−0.000079

The discordance of previous measurements of potentials of cells involving electrolytically prepared silver iodide indicates that its thermodynamic behavior is very uncertain. That this is true might be expected since silver iodide is known to exist in two forms.[40] In this investigation, it was found that chemically precipitated silver iodide behaved in a fairly normal manner, in spite of the fact that it was precipitated under different conditions. The values of electromotive force of cells with electrolytically precipitated silver iodide are higher than those with chemically precipitated silver iodide, which indicates that the latter variety is more stable than the former. The example shows to a marked degree the justification of the use of chemically precipitated salts in cells.

TABLE XIII

THE CELL, Pb (Hg), PbI_2, KI (1 *M*), PbI_2 + AgI, Ag

Temp. °C.	E.m.f. I Volts	$\Delta E/\Delta T$	E.m.f. II Volts	$\Delta E/\Delta T$
25.00	0.20648		0.20629	
		−0.000188		−0.000179
35.00	0.20460		0.20450	
		−0.000186		−0.000183
45.00	0.20274		0.20267	
45.00	0.20261		0.20250	
		−0.000194		−0.000195
35.00	0.20455		0.20445	
		−0.000193		−0.000183
25.00	0.20648		0.20628	
	Mean	−0.000190		−0.000185

In Table XIV are the values for the cell Pb(Hg), PbI_2, KI (0.1 *M*), AgI, Ag. The silver iodide in Cells I and II was precipitated by adding potassium iodide to silver nitrate solution, whereas the silver iodide in Cell III was precipitated by adding silver nitrate solution to potassium iodide solution. The potential of the cells in which 1 *M* potassium iodide was the cell electrolyte is about 1.5 mv. lower than that of the cells with the 0.1 *M* potassium iodide solution. This difference is in that direction, which indicates the tendency for silver iodide to form a double salt with potassium iodide in its more concentrated solutions. This effect, however, does not seem to affect the temperature coefficients.

[40] Fizeau, *Compt. rend.*, **67**, 314 (1864).

TABLE XIV

THE CELL, Pb (Hg), PbI_2, KI (0.1 *M*), AgI, Ag

Temp. ° C.	E.m.f. I Volts	$\Delta E/\Delta T$	E.m.f. II Volts	$\Delta E/\Delta T$	E.m.f. III Volts	$\Delta E/\Delta T$
24.86	0.20789		0.20803		0.20761	
		−0.000189		−0.000190		−0.000187
34.96	0.20598		0.20611		0.20572	
		−0.000195		−0.000197		−0.000188
45.05	0.20401		0.20412		0.20382	
45.05	0.20398		0.20411		0.20378	
		−0.000192		−0.000194		−0.000189
34.96	0.20593		0.20607		0.20569	
		−0.000189		−0.000192		−0.000186
24.86	0.20784		0.20801		0.20757	
	Mean	−0.000191		−0.000193		−0.000188

SUMMARY OF RESULTS

Reactions	*E* Volts	$\Delta E/\Delta T$ Volts/deg.	ΔF Cal.	ΔS Cal./deg.	ΔH Cal.
Hg + $^1/_2$ Cl_2 = HgCl.........	1.0904	−0.000945	....	−21.80	.....
Ag + $^1/_2$ Cl_2 = AgCl.........	1.1362	−0.000595	....	−13.73	.....
Ag + HgCl = AgCl + Hg....	0.0455	0.000338	−1050	7.80	1275
Pb (cryst.) = Pb (Hg)........	0.0057	0.000021	−263	0.97	26
Pb (stick) = Pb (Hg).........	0.0057	0.000015	−263	0.69	−57
Pb (solid) = Pb (Hg).........	0.0057	0.000016	−263	0.74	−42.4
Pb (Hg) + 2AgCl = $PbCl_2$ + 2 Ag......................	0.4843	−0.000202	....	.....	....
Pb (solid) + 2AgCl = $PbCl_2$ + 2Ag...................	0.4900	−0.000186	−22612	− 8.58	−25170
Pb (Hg) + 2HgCl = $PbCl_2$ + 2Hg...................	0.5299	0.000129	....	.....	.....
Pb (solid) + 2HgCl = $PbCl_2$ + 2Hg...................	0.5356	0.000145	−24717	6.70	−22720
Tl (stick) = Tl (Hg)..........	0.0027	0.000020	....	.....	.....
Tl (cryst.) = Tl (Hg).........	0.0024	0.00032	....	.....	.....
Tl (Hg) + AgCl = TlCl + AgCl.......................	0.7766	−0.0000794	....	.....	.....
Tl (cryst.) + AgCl = TlCl + Ag....................	0.7790	−0.000047	−17975	− 1.08	−18296
Pb (Hg) + I_2 = PbI_2.........	0.8936	−0.000042	....	.....	.....
Pb (solid) + I_2 = PbI_2........	0.8993	−0.000026	−41501	− 1.20	−41859
Pb (Hg) + 2AgI = PbI_2 + 2Ag	0.2078	−0.000189	....	.....	.....
Pb (solid) + 2AgI = PbI_2 + 2 Ag......................	0.2135	−0.000173	−9852	− 7.98	−12231

Discussion

The average accuracy of the results for heat content changes calculated from the electromotive data is believed to be better than 30.0 calories per equivalent. For change of entropy the corresponding accuracy is 0.1 entropy unit at 298.0° Å., which is certainly higher accuracy than shown when calculated from existing heat-capacity data.

TABLE XV

	Reaction	ΔS C. p.	ΔS E.M.f.	Diff.
(1)	$Ag + HgCl = AgCl + Hg$	7.7	7.8	+0.1
(2)	$^1/_2Pb + AgCl = {}^1/_2PbCl_2 + Ag$	−4.3	−4.3	0.0
(3)	$Tl + AgCl = TlCl + Ag$	0.9	−1.1	−2.0
(4)	$^1/_2Pb + AgI = {}^1/_2PbI_2 + Ag$	−3.7	−4.0	−0.3

In Table XV will be found a comparison of the entropy changes for 4 reactions, calculated from heat-capacity measurements by Lewis and Gibson and from the data in this paper. The excellent agreement in Reactions 1, 2 and 4 may be somewhat fortuitous, while the disagreement in the third reaction is accounted for to a large extent by too high a value for the entropy of thallous chloride. A reinspection[41] of the heat capacity data for thallous chloride has shown that the previous value obtained by Lewis and Gibson is too high. This conclusion is also compatible with the calculation of the entropy from Latimer's[42] mass equation. The average apparent discrepancy between the entropy change calculated by Lewis and Gibson from specific heats and from the older thermochemical data was 2 entropy units. This difference has now been reduced 10 fold, and thus the present work constitutes a very rigorous test of the third law of thermodynamics.

The heat capacity data for chlorine and iodine are too inaccurate to be of value in testing the third law. However, if its validity be accepted, accurate values for their entropies may be calculated, which are as follows: $^1/_2Cl_2$, $S_{298} = 27.1$;[43] $^1/_2I_2$, $S_{298} = 13.5$.

Summary

1. The technique of making precise measurements of temperature coefficients of electromotive force of galvanic cells has been described.

2. Values for ΔF_{298}, the free energy change; ΔS_{298}, the entropy change; and ΔH_{298}, the change of heat content for certain reactions have been calculated from the measurements of electromotive force and of temperature coefficients of electromotive force of galvanic cells.

3. The third law of thermodynamics has been subjected to a more vigorous test.

4. The entropies of gaseous chlorine and solid iodine have been calculated.

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[41] Lewis, Gibson and Latimer, THIS JOURNAL, **44,** 1008 (1922).

[42] Latimer, *ibid.*, **43,** 818 (1921).

[43] This value for chlorine is to be preferred to 26.3, calculated by Lewis, Gibson and Latimer from a preliminary measurement.