

a measure of the change in pressure which must be applied to counteract the change in randomness produced by a given rise of temperature. Here we may suppose that the distribution of the molecules is constant, being that existing in the crystal. We have recently measured $(\partial P/\partial T)_V$ for solid benzene; it is approximately 23 bars per degree. The coefficient $(\partial P/\partial T)$ along the melting curve is approximately 36 bars per degree.³⁰ For a given rise of temperature, the pressure change necessary to keep constant the distribution in the solid is, according to this argument, more than 1.5 times the pressure change required to keep constant the volume of the solid.

Summary

From measurements of the specific volumes at 25°, the thermal expansions and the compressions of aniline, nitrobenzene, chlorobenzene and bromobenzene, we have been able to compile a table of the volumes of these liquids at any temperature and pressure in the region 25 to 85° and 1 to 1000 bars. Suitable equations for computing the first and second derivatives also are given. From

(30) R. E. Gibson, *THIS JOURNAL*, **56**, 5 (1934); L. Deffet, *Bull. soc. chim. Belg.*, **44**, 71 (1935).

these data the coefficients $(\partial P/\partial T)_V$ and $(\partial E/\partial V)_T$ were computed. Our data enable us to discuss the variation of these and other thermodynamic functions with temperature at constant volume. Both $(\partial P/\partial T)_V$ and $(\partial E/\partial V)_T$ decrease as the temperature increases at constant volume. It is suggested that this effect is due to an increase in the repulsive internal pressure which follows from an increased randomness in the distribution of the molecules in the liquids at higher temperatures. The quantity $(B + P)$ in the Tait equation for the compressibility of the liquids is identified empirically as the repulsive internal pressure. It increases with temperature at constant volume and, when it is combined with the total internal pressure, an estimate of the attractive pressure is made. The attractive pressure so computed is expressible as $P_A = a'V^{-n}$ and is dependent only on the volume within the limits of our experimental error. The exponent n has the value 3 for benzene and 2.74 for the polar liquids.

A weight dilatometer of vitreous silica suitable for the rapid and precise measurements of the thermal expansions of solutions is described.

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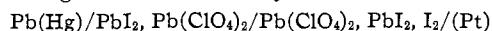
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

A Lead-Iodine Voltaic Cell

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Among the cells made by Gerke¹ the cell



is outstanding in that its temperature coefficient $(\Delta E/\Delta T)$ is as small as that of the saturated Weston cell and the two cells that he made agreed unusually well. These results suggested that the cell might have some value as a standard cell. A number of cells were made and they agreed unusually well with Gerke's cells. They were constant in electromotive force as long as observed and were superior to the Weston cell with respect to recovery from polarization.

The cells were set up in vessels of the type used by Vosburgh and Craig.² Lead amalgam, about 5% lead, was prepared electrolytically. In some of the cells a more dilute amalgam was used by mistake. The iodine was resublimed. Lead iodide and lead chloride were pre-

cipitated from dilute solutions. Lead nitrate was recrystallized. Lead perchlorate solution was prepared by the addition of an excess of lead oxide to a perchloric acid solution, followed by filtration and the addition of enough perchloric acid to give a clear solution.

In the construction of the iodine electrodes, equal quantities of dry lead iodide and iodine were ground, mixed thoroughly and placed in one leg of the cell vessel. Lead perchlorate solution was then introduced to a depth of several centimeters and then lead iodide was allowed to fall through the solution to form a layer about one centimeter thick above the iodine-iodide mixture. A platinum electrode sealed into the end of a glass tube was then introduced carefully into the mixture. In some of the cells a platinum wire in the form of a helix was used for the electrode, but usually the electrode was of platinum foil about 1 sq. cm. in total surface area. The area of the amalgam electrode was about 1 sq. cm. also.

The cells may be divided into three groups. In the first group, Cells 3-16, the materials were not free from oxygen, and air was not excluded. Six of these cells agreed well with each other. Four others were rejected

(1) Gerke, *THIS JOURNAL*, **44**, 1684 (1922).

(2) Vosburgh and Craig, *ibid.*, **51**, 2012 (1929).

because of accidents and four because of disagreement. The disagreement of the last group may be ascribed at least partly to inexperience. In the second group, Cells 17-24, there were no cells rejected. In the construction of these cells the solution was freed from dissolved air and vacuum-nitrogen technique was used for the exclusion of oxygen from the vessel and other materials. In Cells 21 and 22 a saturated lead nitrate solution with excess of solid lead nitrate was used for the electrolyte instead of a lead perchlorate solution, and in Cells 23 and 24 saturated lead chloride solution with excess of solid was used. No significant dependence of the electromotive force on the nature or concentration of the electrolyte was observed. Cells 21-22 and 23-24 became variable when it was attempted to change their temperatures, but they were constant at 25° for over a week and during that time agreed with the perchlorate cells.

Most of the above cells had amalgams that were more dilute than intended. While satisfactory at temperatures below 30°, measurements at higher temperatures showed that the amalgams became unsaturated. Therefore Cells 25-31 were made, and more care was taken that the amalgam was 5% lead. Vacuum technique was not used in their construction, but no cells were rejected. The electromotive forces of the six cells agreed within 0.1 mv. The electromotive forces of all of the satisfactory cells over a period of time are shown in Table I. The average electromotive force agrees well with the value of 0.89363 at 25° found by Gerke.

TABLE I
CONSTANCY OF ELECTROMOTIVE FORCE

Cells	Electrolyte <i>M</i>	$E - 893.00 \text{ mv.}, 25^\circ$				
		1-2 wks.	1 mo.	3	5-6	10
3	0.2	0.54	0.58	0.60	0.59	0.60
6, 7, 13	0.5	.58	.60	.59	.57	.58
15, 16	1.0	.41	.59	.59	.58	.59
17-20	0.5	.58	.58	..	.59	..
21, 22	Satd. ^a	.61
23, 24	Satd. ^b	.51
25-31	1.0	.60	..	.65	.61 ^c	..

^a Lead nitrate solution. ^b Lead chloride solution.
^c Calculated from measurement at 28.5°.

Two series of measurements were made at temperatures other than 25°. Cells 3, 14-16 and 18-20 were measured at 20, 10, 15, 20 and again at 25°, but some of the cells disagreed at 30° and others at higher temperatures, presumably because the amalgams became unsaturated. Cells 25-31 were later measured at 40, 35, 30, 25, 20 and again at 25°. The results are given in Table II. The average change in electromotive force with temperature was 0.000042 v. per degree, which is the value found by Gerke.

TABLE II
CHANGE IN ELECTROMOTIVE FORCE WITH TEMPERATURE

Cells	$-E_{25} - \frac{E_t}{20^\circ}, \text{mv.}$				
	10°	15°	20°	30°	35° 40°
3-20	-0.65	-0.43	-0.22
25-31	-.20	0.20	0.42 0.65

It was found by Niederhauser and Hulett³ that practically all of the polarization of the Weston cell takes place in the mercury limb. Since no mercury salt is present in the lead-iodine cell, it was of interest to test its polarization.

Cell no. 7 was discharged through a resistance of about 150,000 ohms (current 5.3 microamperes) for thirty minutes and the potential drop across the resistance was measured periodically. After fifteen minutes a steady potential difference of 0.89100 v. was attained, which was 2.58 mv. less than the electromotive force of the cell. On breaking the circuit, the electromotive force returned to its original value in twenty minutes. This is typical of the results for several cells discharged through various resistances from 0.1 to 2.5 megohms. Cell 3, discharged for thirty minutes through 9000 ohms, recovered to within 0.01 mv. of its original electromotive force in thirty minutes.

After charging one of the lead-iodine cells for forty-five minutes with a current of 5 microamperes, the cell recovered its original electromotive force in twenty minutes. Measured immediately after the charging was stopped, the electromotive force was 0.3 mv. too high. A normal Weston cell containing a small concentration of acid in the electrolyte when treated in the same manner was still 0.34 mv. too high in electromotive force at the end of thirty minutes. These experiments were repeated on other cells and are believed to be typical.

One cell of larger capacity with electrode areas of about 54 sq. cm. was constructed. The electrode systems were separated by a porous cup. It came to good agreement in electromotive force with the other cells, but later disagreed, presumably because of unequal evaporation of the electrolyte. On discharging through 4000 ohms a constant potential drop across the resistance was attained in twenty minutes and was maintained until measurements were discontinued ten minutes later.

Summary

The cell $\text{Pb}(\text{Hg})/\text{PbI}_2, \text{PbClO}_4(m), \text{PbClO}_4(m), \text{PbI}_2, \text{I}_2/(\text{Pt})$ has been found to be easily reproducible and to remain constant in electromotive force over periods of at least several months. It recovers its original electromotive force after charge or discharge more quickly than the Weston cell.

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(3) Niederhauser and Hulett, *THIS JOURNAL*, **51**, 2332 (1929).