the course of the work. The apparent agreement between the amount of nitrogen and the amount of hexaphenyldigermane, however, has no significance. It results from the fact that the concentrations of the starting solutions were about the same. With more concentrated solution, in general, more hexaphenyldigermane results. The results have been recalulated to a basis of one equivalent weight of sodium triphenylgermanide.

Summary

1. When a solution of sodium triphenylgermanide in liquid ammonia is electrolyzed, the products are hexaphenyldigermane, triphenylgermane and nitrogen.

2. When a platinum anode is used, the quantity of nitrogen corresponds roughly to the amount of triphenylgermane obtained, but when a mercury anode is used, the quantity of nitrogen is markedly smaller than the predicted value. No explanation of this striking difference in behavior can be made at present.

PROVIDENCE, R. I. RECEIVED NOVEMBER 5, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Apparent Molal Isochoric Heat Capacity of Electrolytes[1]

BY FRANK T. GUCKER, JR., AND T. RICHARD RUBIN

Recent studies of the thermal properties of solutions have shown that the apparent molal heat capacity of electrolytes is a linear function of the square root of the concentration over a remarkably wide range, but that individual salts of the same valence type differ considerably both in their slopes and in the limiting values to which they appear to extrapolate at infinite dilution. These facts recently have been summarized and discussed in an article[2] which contains references to the experimental work. All of this was carried out in the usual constant pressure calorimeter, and the apparent molal isopiestic heat capacities alone have been considered. We undertook the present investigation to find out how much the isochoric values differed from the isopiestic ones and to see whether they exhibited any greater regularity among salts of the same valence type.

The difference between the two heat capacities *for 1 cc. of any substance* can be calculated from the well-known thermodynamic equation[3]

$$c_p - c_v = \alpha^2 T/\beta \qquad (1)$$

$$\text{where } \alpha = \frac{1}{V_0}\left(\frac{\partial V}{\partial T}\right)_P \text{ and } \beta = -\frac{1}{V_0}\left(\frac{\partial V}{\partial P}\right)_T$$

are the coefficients of thermal expansibility and of compressibility and T the absolute temperature. V_0 is the volume of the substance under consideration *at atmospheric pressure*. The apparent molal isopiestic and isochoric heat capacities may be defined by the equations

$$\Phi(C_{p2}) = c_p V - c_{p1} V_1 \qquad (2)$$

$$\Phi(C_{v2}) = c_v V - c_{v1} V_1 \qquad (3)$$

where c_p and c_{p_1}, c_v and c_{v_1} are the respective heat capacities *per cubic centimeter* (*not per gram*) of solution and of solvent; V is the volume of solution which contains a mole of solute and V_1 the volume of solvent in which the solute is dissolved. Combination of (1), (2) and (3) gives us the difference between the two apparent molal heat capacities, namely

$$\Delta\Phi(C_2) = \Phi(C_{p2}) - \Phi(C_{v2}) = (\alpha^2 VT)/\beta - (\alpha_1{}^2 V_1 T)/\beta_1 \qquad (4)$$

Calculation of β at 1 Atmosphere.—The calculation of the difference requires a knowledge of the coefficients of expansibility and compressibility at 25° and under one atmosphere pressure. The series of compressibility measurements by Lanman and Mair[4] upon which we based our calculations were made at 25°, but over the pressure range 100 to 300 bars.[5] Our first problem was to reduce these values to atmospheric pressure, and our method was that recently applied by Gibson[6] in his treatment of the properties of solutions under pressure.

It is well known that the compressibility of water decreases as the pressure is increased. The behavior of 1 g. of water can be expressed very satisfactorily by means of a differential equation which Tait suggested in 1888

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(1) Presented at the Cleveland Meeting of the American Chemical Society, September 12, 1934.

(2) Gucker, *Chem. Rev.*, **13**, 111 (1933).

(3) *Cf.* Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 136, for the corresponding equation for 1 *mole* of the substance.

(4) Lanman and Mair, THIS JOURNAL, **56**, 390 (1934).

(5) 1 bar = 10^6 dyne/sq. cm. = 0.9869 atmosphere.

(6) Gibson, THIS JOURNAL, **56**, 4 (1934).

$$-\frac{dv}{dP} = \frac{C}{B + P} \tag{5}$$

where P is the hydrostatic pressure and B and C are experimentally determined constants. B has the same dimensions as P and may be identified with the *internal pressure* in the liquid itself. The *compression* of 1 g. of water between 0 and P is given by the integration of (5)

$$-\Delta_P v = C \ln \left(\frac{B + P}{B}\right) \tag{6}$$

Gibson evaluated the constants from the compression data of Adams[7] and found that equation (6) agreed excellently with these data up to 10 kilobars.[8] Also, equation (5) gave a value of 45.5×10^{-6} reciprocal bars for β at 1 atmosphere, which agrees well with the most recent experimental determinations. We tested the applicability of the equation to the data of Lanman and Mair by calculating, from (6), the mean compressibility coefficient for water between 100 and 300 bars. The value thus obtained was 42.56×10^{-6} reciprocal bars, which agreed well within experimental error with their experimental value of 42.53×10^{-6}. This gave an excellent check on the applicability of the equation and the concordance of the work of these different investigators.

Long ago Tammann pointed out that the properties of solutions were those of water under pressure. Gibson has applied this idea to calculate the compressibility of solutions. When the solution is dilute enough, its compressibility may all be ascribed to its water content. The behavior of 1 g. of solution then may be expressed by the equation

$$-\frac{dv}{dP} = \frac{x_1 C}{B + P_e + P} \tag{7}$$

where x_1 is the weight fraction of water and P_e is a constant (termed the *solute internal pressure*). The *specific compression* is given by the integrated equation[9]

$$-\Delta_P v = x_1 C \ln \left[\frac{B + P_e + P}{B + P_e}\right] \tag{8}$$

We checked the applicability of equation (8) for our purposes in the following way. We calculated the values of P_e for solutions of sodium chloride, using the compression data of Adams,[7] for the pressures 0.5, 1, 1.5, 2 and 3 kilobars. Despite a general tendency for P_e to drop slightly (about 0.03 kilobar) between the lowest and the highest pressures,[10] the *average values* at the three lowest pressures reproduced the observed values of these compressions within the experimental error (which averaged 0.4%, as estimated from the number of significant figures tabulated). Equation (8) therefore agrees well with the facts over this pressure range.[11] We also evaluated P_e from Lanman and Mair's data for sodium chloride between 0.1 and 0.3 kb. When the two series of values were plotted against x_2, the weight fraction of sodium chloride, they were found to agree very satisfactorily. This was additional evidence of the applicability of equation (8). The straight line (Fig. 1) reproduced all the results within 0.5% in the compressibility. Equation (8) was probably even more reliable as we used it in reducing the results of Lanman and

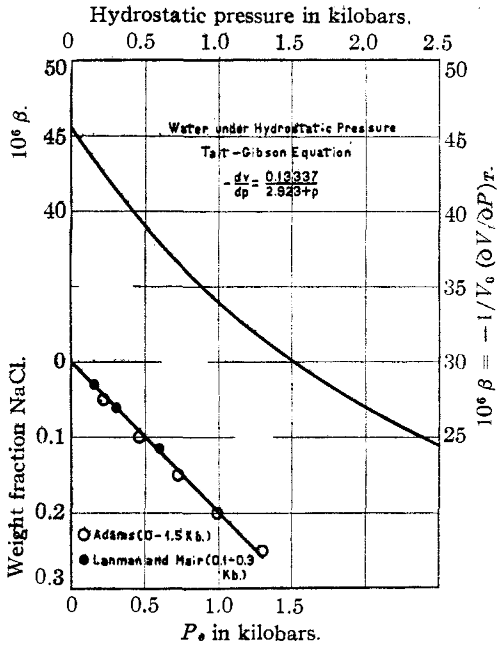

Fig. 1.—The change of the compressibility of water with pressure. The internal pressure of NaCl solutions.

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(7) Adams, THIS JOURNAL, **53**, 3780 (1931).

(8) 1 kilobar = 1000 bars.

(9) For concentrated solutions under high pressure, Gibson suggests that the specific compression is given more exactly by adding to (8) the compression due to the salt. This gives

$$-\Delta_P v = x_1 C \ln \left[\frac{B + P_e + P}{B + P_e}\right] - x_2 \Delta_P v_s \tag{8a}$$

where x_2 is the weight fraction and $-\Delta_P v_s$ the specific compression of the solid salt. This equation gives a slightly higher (and perhaps more logically correct) value for P_e, but was no more satisfactory for our purposes than the less cumbersome (8).

(10) This was equally true when equation (8a) was used in the calculations.

(11) Values of the compressions at 3 kb., calculated from the same values of P_e, differed systematically from the observed by about 0.4%, an amount somewhat larger than the experimental error (about 0.2% at this pressure).

Mair to atmospheric pressure.[12] Knowing the mean coefficient of compressibility per bar ($\bar{\beta}$) between 0.1 and 0.3 kb. and the specific volume (v_0) of the solution at atmospheric pressure, and taking Gibson's values for the coefficients B and C, we could write that the specific compression of the solution ($200v_0\bar{\beta}$) and *internal pressure* (P_e) were related as follows

$$200v_0\bar{\beta} = 0.3071x_1 \log\left[\frac{2.923 + 0.300 + P_e}{2.923 + 0.100 + P_e}\right] \quad (9)$$

We solved this equation for P_e, which we then inserted into the following equation, derived from (7), for β the coefficient of compressibility at atmospheric pressure

$$10^3\beta = \frac{x_1}{v_0} \times \frac{0.13337}{2.924 + P_e}\ (\text{bars}^{-1}) \quad (10)$$

The values of the coefficients of compressibility computed at atmospheric pressure were about 10% greater than those between 100 and 300 bars. It does not seem worth while to tabulate the individual values, but we are including, in Table I, the coefficients A and B of the equation

$$10^6\beta = 45.50 - Ac + Bc^{3/2} \quad (11)$$

which had been shown[13] to be applicable to most electrolytic solutions. This is based upon the linear relationship between the apparent molal compressibility and the square root of the concentration, which we found to hold so exactly for the solutions here discussed. The fact that it holds equally well for the values computed at atmospheric pressure points to the reliability of the methods of calculation outlined above.

TABLE I

SUMMARY OF COEFFICIENTS OF THE EQUATION $10^6\ \beta = 45.50 - Ac + Bc^{3/2}$

Solute	A	B
HCl	1.66	0.26
LiCl	4.97	.84
NaCl	5.91	1.04
KCl	5.73	1.13
LiOH	7.52	1.56
NaOH	8.59	1.90

$\Phi(C_{p_2}) - \Phi(C_{v_2})$ as a Function of $c^{1/2}$.—In order to facilitate the calculation of the difference between the two apparent molal heat capacities at any concentration c (moles solute per liter solution) we can eliminate V_1, between equation (4) and the equation defining the apparent molal volume

$$\Phi(V_2) = V - V_1 = 1000/c - V_1\ (\text{in cc.}) \quad (12)$$

This gives

$$\Delta\Phi(C_2) = T\left[\frac{1000}{c}\left(\frac{\alpha^2}{\beta} - \frac{\alpha_1{}^2}{\beta_1}\right) + \frac{\alpha_1{}^2}{\beta}\Phi(V_2)\right] \quad (13)$$

which, for water solutions at 25°, becomes (in 25° calories)

$$\Delta\Phi(C_2) = 1/c\left(7137\frac{\alpha^2}{\beta} - 10.20\right) + 0.01020\ \Phi(V_2) \quad (13')$$

The last term in this equation is a linear function[14] of $c^{1/2}$. Unfortunately, this is only a small part (15% at most) of the total difference. The other term cannot be expressed as a simple function of $c^{1/2}$ but is readily calculated by evaluating β from the coefficients of equation (11) given in Table I and α from the coefficients of an analogous equation previously published.[15] Values of α and β at even concentrations are given in Table II.

TABLE II

VALUES OF α AND β[a] AT EVEN CONCENTRATIONS

Solute $c^{1/2}$ =	0.25	0.50	0.75	1.00	1.25	1.50
HCl	2.568	2.617	2.711	2.836	2.995	3.189
	4.540	4.512	4.467	4.410	4.341	4.264
LiCl	2.562	2.595	2.638	2.691	2.744	2.790
	4.520	4.437	4.306	4.137	3.937	3.717
NaCl	2.603	2.746	2.959	3.224	3.518	3.822
	4.515	4.415	4.261	4.063	3.831	3.572
KCl	2.595	2.717	2.893	3.104	3.327	3.543
	4.516	4.421	4.275	4.090	3.874	3.642
LiOH	2.576	2.644	2.734	2.830	2.913	2.966
	4.505	4.382	4.193	3.954	3.679	3.388
NaOH	2.618	2.803	3.068	3.380	3.707	4.013
	4.499	4.359	4.147	3.881	3.580	3.261

[a] The *upper* value in each case is $10^4\ \alpha$: the lower is $10^5\ \beta$. $\alpha_1 = 2.550 \times 10^{-4}$, $\beta_1 = 4.550 \times 10^{-5}$. (The fourth place is not significant. but is retained for the sake of self-consistence in the values in Table III.)

Equation (13) is not applicable at zero concentration, since the first term on the right becomes indeterminate (0/0). In this case, however, we can obtain the difference very conveniently in terms of the limiting value of the apparent molal expansibility, $\Phi^\circ\ (E_2)$ and compressibility $\Phi^\circ\ (K_2)$,[16]

$$\Delta\Phi^\circ(C_2) = \frac{\alpha_1 T}{\beta_1}\left[2\Phi^\circ(E_2) - \frac{\alpha_1}{\beta_1}\ \Phi^\circ(K_2)\right] \quad (14)$$

Similarly, we can show that the limiting value of the slope is

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(12) In the case of the *most concentrated* (2.07 *m*) lithium chloride solution. 8 gave 37.93 × 10^{-6} reciprocal bars for β, while the more complicated (8a) gave the almost identical value 37.94.

(13) Gucker, THIS JOURNAL, **55**, 2709 (1933).

(14) Masson [*Phil. Mag.*, [7] **8**, 218 (1929)] and Geffcken [*Z. physik. Chem.*, **A155**, 1 (1931)] showed that the apparent molal volume of most electrolytes is a linear function of $c^{1/2}$ over a wide range of concentration. See also reference 2.

(15) Gucker, THIS JOURNAL, **56**, 1019 (1934), Table III.

(16) For a definition and discussion of these functions, see references 13 and 15.

$$\left(\frac{\partial\,\Delta\Phi(C_2)}{\partial c^{1/2}}\right)_{c\to 0} = \frac{\alpha_1 T}{\beta_1}\left[2\,\frac{\partial\Phi(E_2)}{\partial c^{1/2}} - \frac{\alpha_1}{\beta_1}\,\frac{\partial\Phi(K_2)}{\partial c^{1/2}}\right] \quad (15)$$

Values of the differences in the apparent molal heat capacities at even concentrations are given in Table III and plotted in Fig. 2, along with the limiting slopes tabulated in Table IV.

TABLE III

VALUES OF $\Phi(C_{p_2}) - \Phi(C_{v_2})$ AT EVEN CONCENTRATIONS

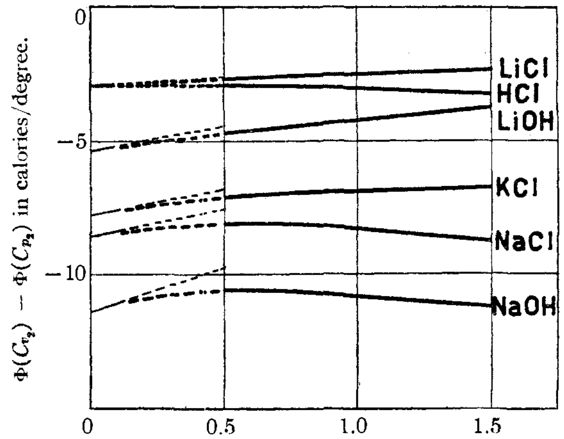
Solute	$c^{1/2} = 0$	0.25	0.50	0.75	1.00	1.25	1.50
HCl	2.90	2.91	2.71	2.85	3.01	3.10	3.23
LiCl	2.94	2.74	2.70	2.57	2.49	2.41	2.31
NaCl	8.60	8.33	8.14	8.11	8.25	8.48	8.71
KCl	7.82	7.32	7.16	6.98	6.89	6.82	6.72
LiOH	5.36	4.92	4.71	4.44	4.23	3.99	3.69
NaOH	11.36	10.66	10.59	10.63	10.78	10.98	11.12

TABLE IV

VALUES OF $\partial\Phi(C_2)/\partial c^{1/2}$ AT ZERO CONCENTRATION

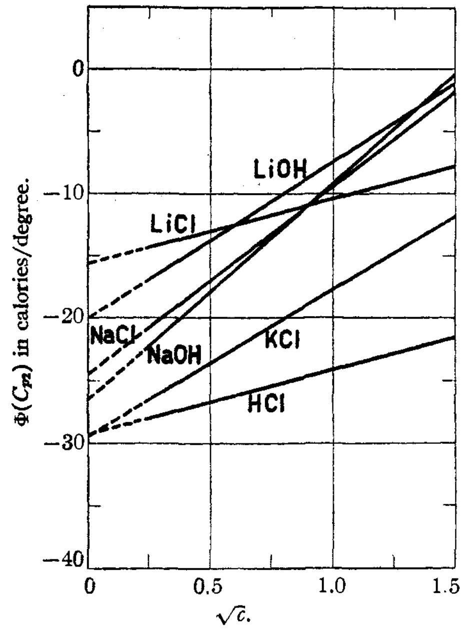
HCl	LiCl	NaCl	KCl	LiOH	NaOH
−0.081	−0.72	−1.94	−2.04	−1.82	−3.27

These curves are all of the same general type, with a *positive* slope for $-\Delta\Phi(C_2)$ in the dilute region, a point of inflection at about a quarter molar and nearly always a negative slope in the more concentrated region, where the line becomes nearly straight again. The limiting tangents and the values at zero concentration are both based upon linear extrapolation of the apparent molal expansibilities and compressibilities, which seems most logical in the light of our present theoretical and experimental knowledge, but has not been verified experimentally. In each case, the expansibility term, which is the less accurately known, is numerically more important. The uncertainty in the position of the curve becomes much less above a quarter molar. Its magnitude depends on the accuracy of the expansibility data. In the case of sodium hydroxide it is about 0.9 calorie units at $c^{1/2} = 0.5$, but only about 0.2 at $c^{1/2} = 1.5$. It is considerably smaller in the case of all the other solutes, except lithium hydroxide, where it is much larger.



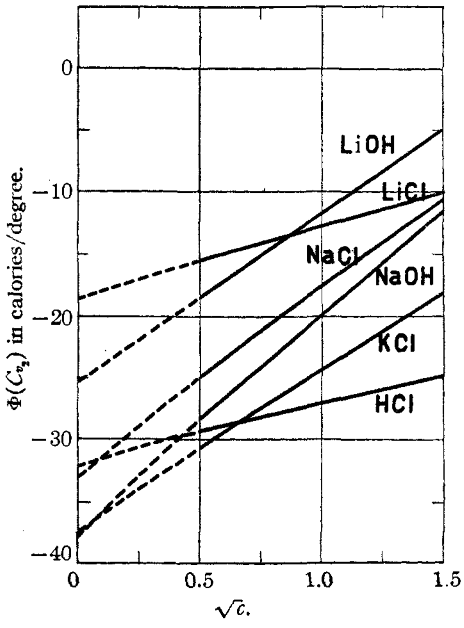
$\sqrt{c}$.

Fig. 2.— $-\Delta\Phi(C_2)$ at 25°.



$\sqrt{c}$.

Fig. 3.—Apparent molal isopiestic heat capacities.



$\sqrt{c}$.

Fig. 4.—Apparent molal isochoric heat capacities.

Perhaps the most striking feature of the curves is the large difference between the apparent molal isochoric and isopiestic heat capacities, in the case of nearly all the solutes. It is often assumed that the thermal properties of solutions are not very different in the isochoric and isopiestic systems, but this proves to be far from true in the case of the solutes investigated.

The apparent molal isopiestic heat capacities are plotted against $c^{1/2}$ in Fig. 3, and the corresponding isochoric ones are similarly plotted in Fig. 4. We have drawn the latter by subtracting the calculated correction from the former, which were drawn straight through the experimental points. However, we do not wish to stress the slight curvature in the isochoric lines. If each experimental isopiestic point had been corrected separately, the resulting isochoric points doubtless would have lain along straight lines, within experimental error.

A comparison of the two plots shows that there is just as much individuality in the positions and slopes of the lines in the isochoric as in the isopiestic systems. We evidently must look elsewhere for the cause of the individuality of the lines, and cannot attribute it to the expansion term since, even in the isochoric system, which lends itself most easily to theoretical treatment, the differences between salts of the same valence type is so striking.

Summary

We have checked the applicability of Gibson's method and used it to reduce the compressibility data of Lanman and Mair to atmospheric pressure.

We have defined the apparent molal isochoric heat capacity $\Phi(C_{v_2})$ and developed equations to calculate it from the corresponding isopiestic quantity $\Phi(C_{p_2})$ and the coefficients of expansibility and compressibility. The limiting values of the difference and of its slope against $c^{1/2}$ are conveniently expressed in terms of the apparent molal compressibilities and expansibilities.

We have computed $\Phi(C_{v_2})$ for six 1-1 electrolytes up to two molal concentration and find it even *more negative* than $\Phi(C_{p_2})$. The difference (3 calorie units for hydrochloric acid and 11 for sodium hydroxide) changes but little with concentration. The values of $\Phi(C_{v_2})$ and the slopes of the $\Phi(C_{v_2}) - c^{1/2}$ curves show as much individuality as those in the isopiestic system.

EVANSTON, ILLINOIS RECEIVED NOVEMBER 5, 1934

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

A Study of the Mechanism of Carbon Dioxide and Hydrogen Peroxide Formation[1]

BY W. F. JACKSON

The accelerating effect of water on the photochemical carbon monoxide-oxygen reaction at high temperatures[2] led to the assumption of a chain mechanism involving hydroxyl radicals and hydrogen atoms. The purpose of the experiments described in the following pages is to gain knowledge of the postulated chain steps

$$\mathrm{OH + CO \longrightarrow CO_2 + H} \tag{1}$$
$$\mathrm{H + O_2 + CO \longrightarrow CO_2 + OH} \tag{2}$$

An electric discharge through moist hydrogen or water vapor provides a reliable source of hydrogen atoms,[3] and there is some evidence that hydroxyl can be drawn from the water discharge.[4] With the hope that the presence or absence of hydroxyl in the products of this discharge could be established in the course of the research, I used it tentatively to examine reaction (1).

Many observations were focused on the formation of hydrogen peroxide, for synthesis of this substance accompanied the carbon monoxide oxidation. These permit a comparison between our work and the more recent study of Rodebush and Wahl.[5]

Experimental Part

Apparatus.—Since the experimental system underwent continual revision throughout the investigation it is impossible to include all the phases of its development. Figure 1 will serve as a reference diagram. Additions

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(1) See G. I. Lavin and W. F. Jackson, THIS JOURNAL, **53**, 383, 3189 (1931). This paper is an abstract of part of the thesis submitted to Princeton University by W. F. Jackson in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Jackson and Kistiakowsky, *ibid.*, **52**, 3471 (1930); Jackson, *ibid.*, **56**, 2631 (1934).

(3) Wood, *Phil. Mag.*, [6] **42**, 729 (1921); **44**, 538 (1922); *Proc. Roy. Soc.* (London), **A97**, 455 (1920); **102**, 1 (1923); Bonhoeffer, *Z. physik. Chem.*, **113**, 199 (1924); Urey and Lavin, THIS JOURNAL, **51**, 3290 (1929).

(4) Lavin and Stewart, *Proc. Nat. Acad. Sci.*, **15**, 829 (1929); Taylor and Lavin, THIS JOURNAL, **52**, 1910 (1930).

(5) Rodebush and Wahl, *J. Chem. Physics*, **1**, 696 (1933).