

# THE CHEMICAL EFFECTS OF PRESSURE

## PART 3.—IONIZATION CONSTANTS AT PRESSURES UP TO 12000 ATM

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The electrical conductances of aqueous solutions of five electrolytes have been measured to 12000 atm at 45° C. Those of ten other electrolytes have been measured to 3000 atm at 25° C. The abnormal conductances of the  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions are found to be increased by pressure.

The conductivity data have been used to derive the pressure dependence of the ionization constants of the bases ammonia, dimethylamine and trimethylamine, and of formic, acetic and propionic acids. The basic ionization constant of ammonia at 45° C is increased from  $1.9 \times 10^{-5}$  mole  $\text{kg}^{-1}$  at 1 atm, to  $1010 \times 10^{-5}$  mole  $\text{kg}^{-1}$  at 12000 atm. This change can be attributed to the greater hydration energies of ions at high pressures.

The first paper of this series<sup>1</sup> described some conductimetric measurements of the basic ionization constants of aqueous ammonia and monomethylamine at pressures between 1 atm and 3000 atm. The ionization constants were greatly increased by pressure and the results suggested that even larger changes should occur above 3000 atm. For that reason we have now extended the pressure range of the measurements on ammonia to 12000 atm.

At the same time, we have investigated the ionization of a number of other weak electrolytes in the original range to 3000 atm: these were the remaining two methylamines and the first three monocarboxylic acids.

## EXPERIMENTAL

**APPARATUS.**—The 3000 atm equipment was described in part 1<sup>1</sup> and the following description relates to the 12000 atm apparatus.

The pressures were produced by a Bridgman intensifier<sup>2</sup> connected to a massive steel cylinder which held the conductivity cell. This cylinder was heated by an external winding and had sufficient heat capacity to permit easy manual control of the internal temperature to within 0.1 deg. over periods of several hours. The temperature was measured by thermometers set in pockets equidistant between the inner and outer walls of the cylinder. Electrical connection to the interior of the cylinder was made through a plug of the type described by Poulter,<sup>3</sup> and this connection was used both in the conductivity measurements and in a preliminary pressure calibration of the intensifier with a manganin resistance gauge (cf. part 2<sup>4</sup>).

We found that glass/platinum conductivity cells never survived compression to 12000 atm. We therefore adopted Jamieson's design<sup>5</sup> for a Teflon/platinum cell, made by mounting platinum electrodes in a hollow Teflon tube and isolating the electrolyte from the pressure fluid (kerosene) by a sliding Teflon plug. The cell had a capacity of 4 ml and a cell constant of  $0.934 \text{ cm}^{-1}$  at 1 atm. The cell constant under pressure was calculated from Bridgman's measurements<sup>6</sup> of the compression of Teflon: it decreased to  $0.881 \text{ cm}^{-1}$  at 12000 atm. The Teflon cell proved completely satisfactory at the highest pressure and had the further advantage over glass cells of being resistant to alkali.

The measurements to 3000 atm were made at 25° C but those to 12000 atm had to be made at 45° C to avoid the freezing of water to ice VI.<sup>7</sup>

**MATERIALS.**—Conductivity water was used throughout. Ammonia and the amines were produced by heating solutions of their hydrochlorides with potassium hydroxide and barium chloride. The gaseous bases were dissolved in water and then redistilled through

a spray-trap into more water. The final solutions were standardized against hydrochloric acid. Analytical grade ammonium chloride, potassium chloride, hydrochloric acid and potassium hydroxide were used without further purification: the potassium hydroxide was found, by analysis, to contain less than 0.8 % of carbonate. The formic, acetic and propionic acids were specimens which had been used in earlier work;<sup>8</sup> their potassium salts were prepared in solution by neutralizing known amounts of the acids with standard potassium hydroxide using an external indicator.

## RESULTS

### ACCURACY

The ionization constants of several of the weak electrolytes were so much increased by pressure as to lie outside the accurate range of conductimetric determinations. For example, 0.01 molal solutions of ammonium hydroxide were more than 60 % ionized at 12000 atm, and the derived ionization constants showed a scatter of  $\pm 20$  %. The reproducibility was much better in the less strongly ionized solutions at lower pressures.

The pressures in the 3000 atm apparatus were known to within 1 %. But those in the 12000 atm bomb had an uncertainty of  $\pm 100$  atm due to frictional effects in the intensifier. Preliminary experiments with a manganin gauge showed that this uncertainty was independent of the total pressure and was therefore relatively more important at low pressures.

### CONDUCTANCES

The conductance of each electrolyte was measured at a number of concentrations and pressures. Altogether several hundred determinations were made, but there is no need to tabulate all these results. Instead, we have summarized them in tables 1 and 2

TABLE 1.—MOLAL CONDUCTANCES OF ELECTROLYTES AND THE SPECIFIC CONDUCTANCE OF WATER TO 12000 ATM AT 45° C

pressure atm	molal conductances/ $\text{ohm}^{-1}$					specific conductance of water ( $\text{ohm}^{-1} \text{cm}^{-1} \times 10^{-6}$ )
	HCl 0.00871	KCl 0.0100	KOH 0.00911	$\text{NH}_4\text{Cl}$ 0.00986	$\text{NH}_4\text{OH}$ 0.01093	
1	523	199	343	199	14.9	1.70
1100	596	209	370	212	25.0	3.07
2500	642	215	392	219	49	5.4
4000	669	211	394	213	83	7.7
5400	683	201	394	204	115	9.4
6800	712	195	404	196	151	11.8
8200	715	183	399	185	185	12.8
9600	718	172	394	172	214	13.4
11000	712	162	389	162	224	15.0
12000	710	152	386	147	248	16.2

TABLE 2.—MOLAL CONDUCTANCES OF ELECTROLYTES TO 3000 ATM AT 25° C

compound	concentration (mole $\text{kg}^{-1}$ )	molal conductances/ $\text{ohm}^{-1}$			
		pressure/atm			
		1	1000	2000	3000
KOH	0.00200	266	283	291	295
$(\text{CH}_3)_2\text{NH}_2\text{OH}$	0.0104	55.2	89.1	125	158
$(\text{CH}_3)_3\text{NHOH}$	0.00985	19.1	33.3	50.5	70.4
KCl	0.0100	140	147	153	151
$(\text{CH}_3)_2\text{NH}_2\text{Cl}$	0.0110	119	121	122	120
$(\text{CH}_3)_3\text{NHCl}$	0.0100	113	119	119	117
HCl	0.00188	420	456	480	496
$\text{HCO}_2\text{H}$	0.0127	45.0	57.0	69.7	80.2
$\text{CH}_3\text{CO}_2\text{H}$	0.0115	15.2	20.5	25.7	31.2
$\text{C}_2\text{H}_5\text{CO}_2\text{H}$	0.0117	12.6	17.4	22.5	27.4
$\text{HCO}_2\text{K}$	0.0105	117	123	123	121
$\text{CH}_3\text{CO}_2\text{K}$	0.00963	105	109	110	109
$\text{C}_2\text{H}_5\text{CO}_2\text{K}$	0.0103	100	102	103	102

by listing a typical set of conductances for each electrolyte, usually at a concentration of about 0.01 molal. The variation of conductance with concentration is only slightly affected by pressure.

The conductances in tables 1 and 2 are described as *molal* conductances because they were calculated from the molal concentrations of the solutes. The values for the specific conductance of water in table 1 are for the water used in these experiments: they are not intended to represent the behaviour of the purest conductivity water.

The only previous measurements of electrolytic conductances above 5000 atm were made by Zisman<sup>9</sup> in Bridgman's laboratory. Our results for KCl and HCl differ from Zisman's by several per cent at 10000 atm. For water, however, the disagreement is much greater and there is little doubt that Zisman's solutions were contaminated with a considerable concentration of unwanted ions, presumably from their direct contact with the kerosene used as pressure fluid.

#### IONIZATION CONSTANTS

The apparent ionization constants  $K'$  were calculated by the method of Davies,<sup>10</sup> Sherrill and Noyes<sup>11</sup> and MacInnes,<sup>12</sup> described in part 1,<sup>1</sup> and they were extrapolated to zero ionic strength to give the thermodynamic ionization constants  $K$ . Tables 3 and 4 list the results, together with the best reported values of  $K$  at 1 atm.

TABLE 3.—IONIZATION CONSTANT OF AMMONIUM HYDROXIDE TO 12000 ATM AT 45° C

pressure/atm	$10^5 K/\text{mole kg}^{-1}$	pressure/atm	$10^5 K/\text{mole kg}^{-1}$
1	1.93 (1.88)*	6800	211
1100	5.03	8200	377
2500	18.2	9600	620
4000	48	11000	770
5400	113	12000	1010

\* Everett and Landsman.<sup>13</sup>

TABLE 4.—IONIZATION CONSTANTS OF VARIOUS ACIDS AND BASES TO 3000 ATM AT 25° C

electrolyte	$10^5 K/\text{mole kg}^{-1}$			
	pressure/atm:			
	1	1000	2000	3000
HCO <sub>2</sub> H	17.4 (17.7)*	24.4	32.5	41.8
CH <sub>3</sub> CO <sub>2</sub> H	1.71 (1.75)*	2.70	3.91	5.38
C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> H	1.26 (1.34)*	2.06	3.14	4.44
NH <sub>4</sub> OH†	1.75 (1.76)‡	5.11	12.2	24.3
(CH <sub>3</sub> )NH <sub>3</sub> OH†	41.9 (42.5)§	118	257	464
(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> OH	58.9 (59.9)§	162	366	752
(CH <sub>3</sub> ) <sub>3</sub> NHOH	6.28 (6.31)§	18.0	43.3	91.5

\* Harned and Owen.<sup>14</sup>

† part 1 of this series.<sup>1</sup>

‡ Everett and Landsman.<sup>13</sup>

§ Everett and Wynne-Jones.<sup>15</sup>

## DISCUSSION

### CONDUCTANCES

Apart from their use in deriving ionization constants, the conductances listed in table 1 are interesting in themselves.

1. STRONG SALTS.—The values of the molal conductances of KCl and NH<sub>4</sub>Cl are first increased slightly and then reduced by pressure. This behaviour is characteristic of solutions of strong salts,<sup>9, 16</sup> and arises from two competing effects: compression increases the number of ions in a unit volume of the solutions, but at the same time it reduces the mobility of the ions by raising the viscosity of water.<sup>17</sup>

2. STRONG ACIDS AND BASES.—Zisman<sup>9</sup> and Baughan<sup>18</sup> have already commented on the abnormal behaviour of compressed HCl solutions, whose molal conductances  $\Lambda'$  are almost constant above 5000 atm. Our measurements have

confirmed Zisman's results and shown that solutions of KOH behave in the same way. This is clearly seen in fig. 1, where  $\Lambda'_{\text{HCl}} - \Lambda'_{\text{KCl}}$  and  $\Lambda'_{\text{KOH}} - \Lambda'_{\text{KCl}}$  have been plotted against pressure.

These two quantities are rough measures of the excess conductances of the  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions, that is, of the amounts by which their conductances exceed those of similarly sized ions which move by normal diffusion in the electric field.

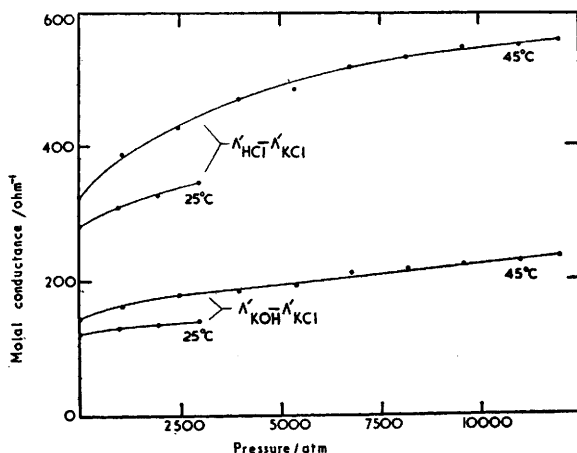
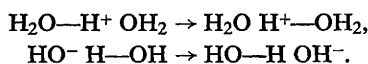


Fig. 1.—The excess conductances of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  at high pressures.

There is little doubt that the excess conductances of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  in water are proportional to the rates of the proton exchanges:



Adopting Bell's model for proton-transfer reactions,<sup>19</sup> we suggest that pressure assists these exchanges because it provides some of the repulsion energy needed to bring the oxygen atoms close enough for a proton switch to occur.

#### IONIZATION EQUILIBRIA

The effect of pressure on the ionization of a weak electrolyte is conveniently represented by the difference between the standard free energy of ionization at a pressure  $p$ ,  $\Delta\bar{G}_p^\circ$  and the corresponding quantity at atmospheric pressure,  $\Delta\bar{G}_1^\circ$ .\* This difference is given by the relation:

$$\Delta\bar{G}_p^\circ - \Delta\bar{G}_1^\circ = -RT \ln (K_p/K_1).$$

If the  $K$ 's are in molal units, as they are here, then the standard state of the solutes is that of unit molal activity. We have calculated  $\Delta\bar{G}_p^\circ - \Delta\bar{G}_1^\circ$  from the data in tables 3 and 4, and plotted the results against pressure in fig. 2.

We showed in part 1 that the decrease of  $\Delta\bar{G}_p^\circ - \Delta\bar{G}_1^\circ$  for the ionization of ammonium hydroxide between 1 and 3000 atm could be accounted for by assuming that it represented the change in hydration free energy of the  $\text{NH}_4^+$  and  $\text{OH}^-$  ions under pressure, and that this change could be calculated from Born's formula<sup>20</sup> as modified by Latimer, Pitzer and Slansky.<sup>21</sup> It is interesting now, to test this model above 3000 atm.

Unfortunately, the dielectric constant of water which is needed in the calculations, has been measured to only 3000 atm.<sup>22</sup> The best that can be done is

\* Throughout this paper the subscripts 1 and  $p$  indicate that the associated quantities are for the pressures 1 atm and  $p$  atm.

to extrapolate the low pressure results by an equation which Owen and Brinkley<sup>23</sup> found satisfactory for other polar liquids to 12000 atm. This is:

$$1 - \frac{D_1}{D_p} = AD_1 \log_{10} \left( \frac{B+p}{B+1} \right)$$

where  $D$  is the dielectric constant and  $A$  and  $B$  are parameters calculated from the measurements of Kyropoulos to 3000 atm.<sup>22</sup> In view of the uncertainty of this extrapolation there seems little point in continuing to use Latimer, Pitzer and Slansky's refinement of Born's model. We have therefore returned to the original Born formula for the molar energy of hydration of singly charged ions of radius  $r$ ,

$$\Delta G_h = -\frac{Ne^2}{2r} \left( 1 - \frac{1}{D} \right),$$

where  $N$  is Avogadro's number.

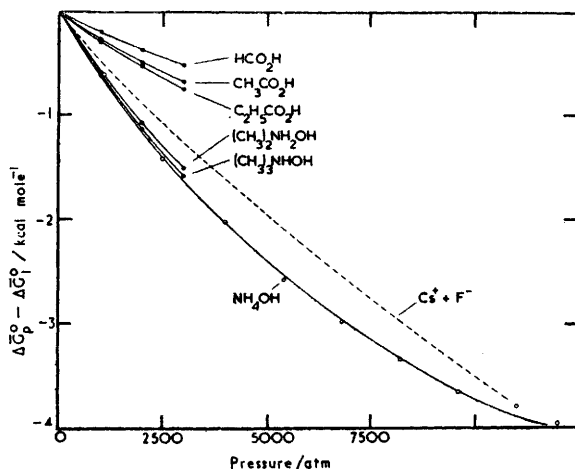


Fig. 2.—The pressure dependence of the ionization of weak electrolytes. The dotted curve represents the theoretical hydration energies of the ions  $\text{Cs}^+ + \text{F}^-$ . The curve for ammonium hydroxide is for 45° C: all the others are for 25° C.

It is not possible to apply this relation directly to the ions  $\text{NH}_4^+$  and  $\text{OH}^-$  at high pressures, because their compressibilities are not known. Instead, we have considered the ions  $\text{Cs}^+$  and  $\text{F}^-$  whose radii are similar to those of  $\text{NH}_4^+$  and  $\text{OH}^-$ , and whose compressibilities can be estimated from Bridgman's measurements of the volume of crystalline caesium fluoride to 12000 atm.<sup>24</sup> We have assumed that the two ions are equally compressible. The calculated free energies of hydration are listed in table 5 and plotted against pressure in fig. 2.

TABLE 5.—BORN ENERGY OF HYDRATION OF  $\text{Cs}^+ + \text{F}^-$  AT 45° C

pressure/atm	1	2000	4000	6000	8000	10000	12000
$D_p$ for water	71.8	78.9	84.3	88.9	93.0	96.7	100.1
relative ionic radius, $r_p/r_1$ *	1	0.9973	0.9947	0.9923	0.9901	0.9879	0.9860
$\Delta G_h$ for $\text{Cs}^+ + \text{F}^-$ / kcal mole <sup>-1</sup>	-216.9	-217.8	-218.5	-219.2	-219.8	-220.4	-220.9
$(\Delta G_h)_p - (\Delta G_h)_1$ / kcal mole <sup>-1</sup>	0	-0.9	-1.6	-2.3	-2.9	-3.5	-4.0

\*  $r_1$  is 1.69 Å for  $\text{Cs}^+$ , and 1.36 Å for  $\text{F}^-$ .

The agreement between theory and experiment (fig. 2) is as good as could be expected from the crudeness of the calculations.

We suggested earlier<sup>1</sup> that the effect of pressure on the ionization of a weak electrolyte might vary inversely with the size of its ions. This suggestion, based on Born's formula, involved a number of assumptions which were explicitly stated, and also an implicit assumption that in a series of ions of different sizes, the ratio of compressibility to volume does not increase with the size of the ions. If these assumptions were correct the order of the pressure effects for the methyl-ammonium hydroxides would be:



The first two bases were found to conform to this sequence.<sup>1</sup> But our present measurements show that the last two certainly do not. The actual order of pressure effects is:



It is possible that we are not justified in ignoring the effect of pressure on the hydration of the un-ionized amines.

Fig. 2 shows that the carboxylic acids are much less strengthened by pressure than are ammonia and the amines. This effect may be related to the diffuseness of charge in the carboxylate ions.

#### CHANGES OF VOLUME ON IONIZATION

The change in partial molar volume for the ionization of a weak electrolyte is given by the relation:

$$\Delta \bar{V}_p^\circ = \partial \Delta \bar{G}^\circ / \partial p.$$

The slopes of the curves in fig. 2 are therefore equal to the values of  $\Delta \bar{V}_p^\circ$  for the several electrolytes. The limiting slopes at 1 atm should be the same as  $\Delta \bar{V}_1^\circ$ , calculated from the densities of solutions of the weak electrolytes and of their salts at atmospheric pressure. Table 6 shows that this is so.

TABLE 6.—THE VOLUME CHANGE FOR IONIZATION OF WEAK ELECTROLYTES AT 1 ATM AND 25° C

electrolyte	$\Delta \bar{V}_1^\circ / \text{cm}^3 \text{ mole}^{-1}$	
	from pressure dependence of ionization constants	from density measurements at 1 atm*
HCO <sub>2</sub> H	— 8.8	— 8.0
CH <sub>3</sub> CO <sub>2</sub> H	—12.2	—12.5
C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> H	—12.9	—13.7
NH <sub>4</sub> OH	—28.9†	—30.0‡
(CH <sub>3</sub> )NH <sub>3</sub> OH	—26.4†	—27.5
(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> OH	—27.2	—27.4
(CH <sub>3</sub> ) <sub>3</sub> NHOH	—28.1	—28.1

\* Hamann and Lim.<sup>8</sup>

† part 1.1

‡ This value is for 20° C.

Finally, to illustrate the way in which  $\Delta \bar{V}_p^\circ$  changes with pressure, we quote the following values for the ionization of ammonium hydroxide at 45° C:

pressure/atm	1	2500	5000	7500	10000
$\Delta \bar{V}_p^\circ / \text{cm}^3 \text{ mole}^{-1}$	— 28.5	— 19	— 14	— 10	— 7

We are indebted to Mr. H. G. David for designing the high pressure equipment and to Mr. S. J. Lake for assembling and maintaining it.

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  - <sup>20</sup> Born, *Z. Physik*, 1920, **1**, 45.
  - <sup>21</sup> Latimer, Pitzer, and Slansky, *J. Chem. Physics*, 1939, **7**, 108.
  - <sup>22</sup> Kyropoulos, *Z. Physik*, 1926, **40**, 507.
  - <sup>23</sup> Owen and Brinkley, *Physic. Rev.*, 1943, **64**, 32.
  - <sup>24</sup> Bridgman, *Proc. Amer. Acad. Arts. Sci.*, 1932, **67**, 345.
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