Summary.

(1) With a new and improved form of pyknometer we have determined the density of salts and other substances with an accuracy of 3 or 4 units in the fourth decimal place, that is, within 0.02%. In many cases, however, such accuracy is unnecessary since the variations of density due to inhomogeneities of the material may be much greater than this.

(2) Powdering a crystallin substance does not change its density by an amount which we can detect with certainty, provided that the material is homogeneous and free from cracks and holes; but if the substance is not homogeneous, then, as might be expected, the fine powder is denser than the coarse particles.

(3) Neither does very high hydrostatic pressure produce any aftereffect on the density of strictly homogeneous crystallin compounds.

(4) But if the pressure be not uniform, then the density of a metal which has been subjected to such compression—or has been deformed in any other way—usually increases first (owing presumably to the filling up of pores and cracks) and then decreases, sometimes even so as to reach a final density less than the original value. Subsequent annealing of the specimen causes a renewed increase of density. The direction of the change of density on compressing bismuth is, contrary to Spring's conclusion, the same as that for other metals, namely a decrease of density following upon deformation. The bearing of these results upon the question of the "flow" of metals is discussed: they are shown to be in harmony with the idea that the "flow"—or indeed any deformation—of a metal is a manifestation of a real melting produced by the unequal strains set up during the process.

(5) Finally it is important to emphasize the fact that the density of most substances is somewhat variable, owing to a lack of complete homogeneity of the material. In consequence of this, slight changes of density cannot be regarded as good evidence for the occurrence of any transformation or chemical reaction—whether produced by subjecting the system to compression or by other means.

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THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF THE ALCOHOLS IN LIQUID HYDROGEN CHLORIDE.

BY E. H. ARCHIBALD.

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In previous papers,[1] results have been given of a study of the electrical conductivity of solutions of the alcohols in liquid hydrogen bromide, and of the organic acids in liquid hydrogen chloride and bromide. These

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[1] THIS JOURNAL, 29, 665 (1907); 29, 1416 (1907).

results showed that in these solvents the variation of the molecular conductivity with dilution over a considerable range of concentration was abnormal; as shown for other organic compounds in these solvents by Steele, McIntosh and Archibald,[1] in that the molecular conductivity increased with the concentration rather than with the dilution, as is the case with almost all aqueous solutions. As regards the solutions of the organic acids in hydrogen chloride, it was found that when the solutions examined became very dilute, the molecular conductivity-dilution curve changed its direction and continued to show the usual variation. In several cases these curves showed both maximum and minimum values for the molecular conductivity, notably for solutions of salicylic acid in the hydrogen chloride. Other cases of such variations in the molecular conductivity-dilution curve have been noted,[2] in particular by Franklin and Gibbs[3] for solutions of silver nitrate in methyl amine and of various bromides in liquid sulfur dioxide: also by Schlesinger and Calvert[4] for solutions of ammonia in formic acid. It was further found that in the case of the solutions of the organic acids, the hydrogen chloride formed much better conducting solutions than the hydrogen bromide.

It seemed well worth while to study some typical solutions of alcohols in liquid hydrogen chloride, to ascertain the nature of the variation of the molecular conductivity with dilution for solutions as dilute as could be examined. An attempt was also made to follow the conductivity of some of these solutions from pure hydrogen chloride through various concentrations of alcohol to pure alcohol. The results obtained are set forth below.

The preparation of the pure liquid hydrogen chloride and of the alcohols has been described in the papers cited above. The very small conductivity of the solvent, 0.02×10^{-6}, was strong evidence of its purity. Particular attention was paid to keeping water out of the pure liquid chloride solutions while the measurements were being made.

The method of measuring the resistance of the solutions was that of Kohlrausch, involving the use of the Wheatstone bridge, alternating current and telephone receiver. The conductivity vessels were of the "dip" variety, as previously described. Careful attention to the platinizing of the electrodes ensured a very satisfactory "minimum" in the telephone. Two sets of electrodes were used, one for solutions having a high, the other for solutions having a low resistance. The resistance capacities

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[1] *Phil. Trans.*, (*A*) 205, 99 (1905).

[2] Kablukov, *Z. physik. Chem.*, 4, 429 (1889). Plotnikov, *J. Russ. Phys. Chem. Soc.*, 34, 466 (1902); 35, 794 (1903). Sakur, *Ber.*, 35, 1242 (1902). Kahlenburg and Ruhoff, *J. Phys. Chem.*, 1, 284 (1903). Walden, *Z. physik. Chem.*, 54, 131 (1906).

[3] THIS JOURNAL, 29, 1389 (1907); *J. Phys. Chem.*, 15, 675 (1911).

[4] THIS JOURNAL, 33, 1924 (1911).

of the cells were determined by measuring the conductivity of 0.01 and of 0.02 *N* solutions of potassium chloride.

Outside leak of current from one lead to the other due to the formation, on the outside of the conductivity vessel, of a film of aqueous solution of hydrochloric acid of very high conductivity, must be carefully guarded against, when working with dilute solutions in the hydrogen chloride.

The temperature of the bath of solid carbon dioxide and ether, in which the conductivity vessel was immersed, was kept at —89° by connecting the bath with a good water pump, and regulating the pressure over the carbon dioxide-ether mixture. The temperature was indicated by a pentane thermometer graduated to tenths of a degree.

The results obtained with the different alcohols are set forth in the tables below. We give in Table I the values found for the solutions actually measured and in Table II the values for the round concentrations. The dilutions are the number of liters containing one gram molecule of solute, the conductivity values are expressed in reciprocal ohms.

TABLE I.—SOLUTIONS IN LIQUID HYDROGEN CHLORIDE.

Methyl alcohol.		Ethyl alcohol.		Butyl alcohol.		Resorcinol.	
Dilution.	Molecular conductivity.	Dilution.	Molecular conductivity.	Dilution.	Molecular conductivity.	Dilution.	Molecular conductivity.
33.2	0.0528	48.8	0.0191	29.4	0.0238	12.64	2.930
15.19	0.0405	23.7	0.0182	11.1	0.0151	6.29	3.430
13.42	0.0395	12.19	0.0185	5.07	0.0178	4.09	3.770
8.31	0.0420	7.48	0.0200	3.21	0.0219	2.19	4.110
4.40	0.0528	4.66	0.0216	2.23	0.0244	1.222	4.270
2.91	0.0721	3.50	0.0268	1.53	0.0359	0.874	3.870
2.26	0.0981	2.58	0.0305	1.266	0.0638	0.681	3.610
1.608	0.1558	1.93	0.0378	0.944	0.0755	0.539	3.040
1.321	0.2282	1.48	0.0491	0.730	0.1262	....	...
1.056	0.3520	1.13	0.0798	0.574	0.2290	....	...
0.864	0.511	0.881	0.1405	0.336	0.442	....	...
0.649	0.832	0.713	0.267	0.272	0.470	....	...
0.694	1.190	0.591	0.361	0.2163	0.445	....	...
0.379	1.498	0.507	0.505	0.1613	0.332	....	...
0.273	1.622	0.423	0.645	0.1333	0.1173	....	...
0.201	1.587	0.332	0.799	....	....	....	...
0.156	1.457	0.263	0.902	....	....	....	...
0.130	1.199	0.173	1.155	....	....	....	...
....	....	0.156	1.045	....	....	....	...
....	....	0.131	0.878	....	....	....	...
....	....	0.120	0.803	....	....	....	...

As stated above, attempts were made to carry the measurements through the concentrated solutions of the alcohols in the liquid hydride, to pure alcohol. These attempts were, however, not entirely successful. The temperature coefficients of the conductivity for the concentrated solutions are so large that it is exceedingly difficult to obtain accurate measurements. In the case of the methyl alcohol a compound separates out when about equal parts by weight of solute and solvent are present, and finally the whole mass solidifies. We hope soon to study these solutions from the other side, *viz.*, to measure the conductivity of the solutions of hydrogen chloride in alcohol, at temperatures corresponding to those obtaining in the above measurements.

Regarding these measurements of the concentrated solutions, we may say that on each side of the mixture which corresponds to the compound which separates out, the specific conductivity remains practically constant over a wide variation in the concentration, as the solution is diluted either with liquid hydrogen chloride or with alcohol. This is true of both the methyl and ethyl alcohol solutions. The maximum specific conductivity is about three times as great as that of 0.02 *N* potassium chloride at 18° C., *viz.*, about 0.00715 reciprocal ohms.

For the sake of comparison we give in Table II the values of the molecular conductivity for round concentrations, obtained from the curves given by the values in Table I.

TABLE II.—SOLUTIONS OF THE ALCOHOLS IN LIQUID HYDROGEN CHLORIDE.
Molecular Conductivity.

Dilution.	Methyl alcohol.	Ethyl alcohol.	Butyl alcohol.	Resorcinol.
50.0	....	0.0191	....	...
35.0	0.0540	0.0185	....	...
30.0	0.0500	....	....	...
25.0	0.0452	0.0182	....	...
20.0	0.0420	....	....	...
15.0	0.0398	0.0183	....	2.852
10.0	0.0405	0.0190	0.0155	3.100
7.50	0.0435	0.0200	....	3.281
5.00	0.0502	0.0215	0.0180	3.670
2.50	0.0906	0.0271	0.0235	4.050
2.00	0.1260	0.0367	0.0275	4.140
1.50	0.1785	0.0479	0.0365	4.200
1.00	0.392	0.1055	0.0630	4.100
0.750	0.640	0.2060	0.1245	3.640
0.500	1.172	0.503	0.2920	2.910
0.250	1.624	0.955	0.465	...
0.150	1.470	1.048	0.261	...
0.1	1.060	0.704	....	...

The results for methyl, ethyl and butyl alcohol are shown graphically in Fig. 1, where, following the suggestion of Franklin, the logarithms of the dilutions are plotted as abscissas and the molecular conductivities as ordinates.

It may first be noted that here as in the case of the solutions of the alcohols in liquid hydrogen bromide, the lower the alcohol in the series the better conducting solution it forms; while the resorcinol gives solutions which conduct better than those formed from the alcohols of the paraffin series, as was the case with the hydrogen bromide solutions.

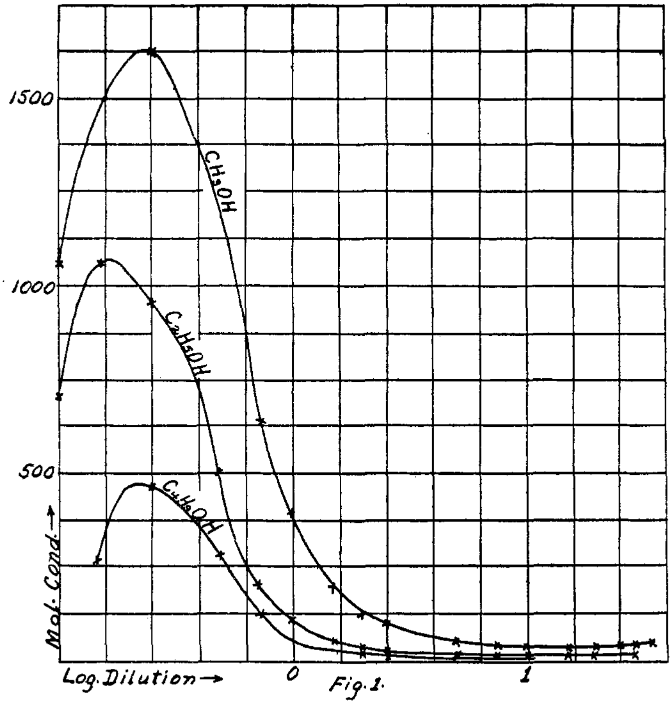

Fig. 1.

Before discussing these results further, we will give the values of the temperature coefficients of the conductivity found for the hydrogen chloride solutions. These are shown in Table III, expressed as percentage values of the conductivity at the lower temperature. The dilutions of the particular solutions are also shown, together with the temperatures between which the measurements were made.

TABLE III.—HYDROGEN CHLORIDE SOLUTIONS; TEMPERATURE COEFFICIENTS OF CONDUCTIVITY.

Dilution.	Temp. limits.	Methyl alcohol. Per cent	Ethyl alcohol. Per cent	Butyl alcohol. Per cent	Resorcinol. Per cent
137.0	—88.8 and —85.4	..	...	..	—1.33
6.29	—88.5 and —85.5	..	...	..	0.00
5.07	—89.3 and —85.8	..	...	5.23	..
4.66	—88.5 and —85.5	..	3.9	..	..
2.91	—89.0 and —86.0	1.21	...	..	..
1.06	—89.0 and —86.0	2.68	...	..	..
0.591	—88.0 and —85.0	..	4.0	..	..
0.574	—89.0 and —85.3	..	...	6.5	..
0.539	—89.0 and —85.0	..	...	..	+1.3

With regard to these temperature coefficients, we notice that the less the conducting power of the alcohol, the greater is the variation in the conductivity with temperature; while the temperature coefficient of the more dilute solution, and, therefore, of the poorer conducting solution of any one alcohol is less than that of the more concentrated. The solutions of the resorcinol are particularly interesting in this respect. Here we have rather good conducting solutions with negative temperature coefficients for the dilute solutions, and positive for the more concentrated. This behavior may be explained as follows: With rise of temperature presumably the fluidity will increase and the ionization will decrease. The first change will cause the conductivity to increase, the second will cause it to decrease. It seems as if for the concentrated solutions the effect of the change in viscosity overbalances that due to the change in ionization giving positive although small temperature coefficients; while for the dilute solutions the converse holds true, the effect due to the decrease in ionization overbalances the effect due to the change in fluidity, and we observe a negative temperature coefficient.

In like manner, by assuming a large change in the viscosity with change in temperature for the other solutions, we can explain the large temperature coefficients of conductivity; and this change will naturally be greater for the concentrated solutions than for the dilute, which is in accordance with the fact that the temperature coefficients are greater for the concentrated than for the dilute solutions. This point will be referred to again later.

Referring now to the values for the molecular conductivity in Table II, we note that for the more dilute solutions of methyl and ethyl alcohol the molecular conductivity varies with the dilution in the usual manner; *viz.*, it increases with the dilution as was observed in the case of the more dilute solutions of the organic acids in liquid hydrogen chloride. However, for dilutions below 15 liters per gram molecule, the molecular conductivity increases with the concentration, until it reaches a value about fifty times as great as its minimum value; it then decreases with the concentration quite rapidly for all the remaining measurements.

With regard to the curves shown in Fig. 1, they are very similar to the corresponding curve for solutions of salicylic acid in liquid hydrogen chloride; and in many respects to the curves obtained by Franklin for methylamine solutions of silver nitrate, and sulfur dioxide solutions of potassium bromide and iodide; except that for the solutions in the liquid hydrogen chloride, the increase of molecular conductivity with concentration is much more marked.

Lewis and Wheeler[1] have suggested that the increase of the molecular

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[1] *Proc. Am. Acad.*, 41, 419.

conductivity with the concentration, in the case of weak ionizing solvents, may be due to autoionization of the solute. Franklin[1] explains his results with the methylamine and sulfur dioxide solutions in a similar way. He also explains the rise in the molecular conductivity shown for the first part of the curve—that for the concentrated solutions—by assuming that the increase in the conductivity with dilution, due to the decrease in the viscosity, is great enough for these concentrated solutions to overbalance the effect due to autoionization; while for the other end of the curve the increase in molecular conductivity with dilution is occasioned by the usual increase in ionization due to the solvent.

With regard to the solutions of the organic acids and alcohols in the liquid hydrides, similar explanations to those given by Franklin seem not unlikely to apply to the variation in the molecular conductivity at the two extreme ends of the curves, but for the greater part of the curve where the molecular conductivity is increasing rapidly with the concentration, some other explanation must be found, as it seems unlikely that in the case of a weak ionizing substance such as ethyl alcohol, autoionization would take place to a sufficient extent to cause the molecular conductivity to increase to fifty times its value between a dilution of 7.0 and 0.20 liters per gram molecule. The explanation offered by Steele, McIntosh and Archibald[1] for this abnormal behavior in the case of the solutions in the liquid halogen hydrides seems more likely to apply to the measurements recorded in this paper. This explanation assumes that there is a compound formed in solution between solvent and solute and that this compound which contains n molecules of solute is the electrolyte which is ionized. The concentration of the electrolyte is then proportional to the nth power of the concentration of the dissolved substance, while the molecular conductivity will be given by the expression kv^n rather than by kv; where k is the specific conductivity and v the dilution of the solution in question.

The author has shown in previous papers, that when the molecular conductivity is computed according to this assumption for solutions of the alcohols and organic acids in the liquid halogen hydrides any one value of n for a certain solute is applicable only over a narrow range of dilution, indicating that the composition of the electrolyte varies with the concentration of the solution. The same variation seems to hold in the present instance. For the more dilute of the solutions examined the value of n must be 1 while over a considerable range the value $n = 4$ would seem very probable. Thus for methyl, ethyl and butyl alcohols the values of kv^4 for several dilutions are found in Table IV.

The same value of n applied to more dilute or more concentrated solutions would give almost impossible values. This is but additional evidence

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[1] *Loc. cit.*

that a solution is a much more complicated system than we usually suppose.

TABLE IV.

Dilutions.	Methyl alcohol. kv^4.	Ethyl alcohol. kv^4.	Butyl alcohol. kv^4.
2.50	1.395	0.421	0.363
2.00	1.008	0.293	0.220
1.50	0.599	0.161	0.123
1.00	0.392	0.105	0.063
0.75	0.268	0.085	0.052
0.50	0.146	0.062	0.036
0.25	0.025	0.015	0.007

It is interesting to compare the conductivity of the hydrogen bromide solutions of the alcohols with corresponding solutions in the hydrogen chloride. These are shown in Table V. The values for acetic acid in the two solvents are also included.

TABLE V.—MOLECULAR CONDUCTIVITY VALUES FOR HYDROGEN BROMIDE AND CHLORIDE SOLUTIONS.

	Hydrogen bromide solutions.				Hydrogen chloride solutions.			
Dil.	Methyl alcohol.	Ethyl alcohol.	Resorcinol.	Acetic acid.	Methyl alcohol.	Ethyl alcohol.	Resorcinol.	Acetic acid.
10.0	...	0.00048	0.076	0.0068	0.0405	0.019	3.10	0.236
5.0	0.00068	0.00050	0.127	0.0184	0.050	0.021	3.67	0.387
2.0	0.00166	0.00100	0.252	0.124	0.126	0.037	4.14	0.769
1.0	0.00925	0.00465	0.351	0.332	0.392	0.105	4.10	1.11
0.5	0.211	0.100	...	....	1.172	0.503	2.91	...
0.25	0.631	...	...	....	1.62	0.955	..	...

For the dilute solutions, we see that the hydrogen chloride solutions conduct between 50 and 100 times better than the solutions in hydrogen bromide, but as the concentration increases the conducting power of the different solutions becomes more nearly equal. This is due to the much greater increase in the molecular conductivity of the hydrogen bromide solutions with concentration.

Summary.

We may briefly summarize the foregoing results as follows:

(1) The conductivity of hydrogen chloride solutions of methyl, ethyl and butyl alcohols, and of resorcinol have been measured, and the temperature coefficients of the conductivity of these solutions have been determined at different concentrations.

(2) For the dilute solutions of the methyl, ethyl and butyl alcohols the molecular conductivity increases with the dilution, and this is also the case for the more concentrated solutions of all four solutes, but for a wide range of dilution the molecular conductivity increases with the concentration rather than with the dilution.

(3) The increase in the molecular conductivity with the dilution for

the concentrated solutions has been explained by assuming a considerable increase in the viscosity of the solution as the concentration increased with a corresponding decrease in the mobility of the ions.

(4) The decrease in the molecular conductivity with dilution over the greater part of the curve plotted in Fig. 1 is explained by assuming a complex electrolyte, containing n molecules of solute. The expression for the molecular conductivity is then kv^n rather than kv.

(5) The best conducting solution for the above solutes has a specific conductivity of 0.007 reciprocal ohms.

(6) The temperature coefficients for ethyl and butyl alcohols are very large and increase with the concentration. This is explained by assuming a large decrease in the viscosity of the solution with the temperature, this decrease being greater the more concentrated the solution. In the case of resorcinol the effect of the decrease in viscosity with temperature is great enough to change a negative temperature coefficient for a dilute solution, to a positive coefficient for a concentrated solution.

(7) The molecular conductivities of the above alcohols and of acetic acid in liquid hydrogen bromide and chloride are compared, the hydrogen chloride solutions being much the better conductors.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE ATOMIC WEIGHT OF FLUORINE.

[PRELIMINARY PAPER.]

BY D. J. MCADAM, JR., AND EDGAR F. SMITH.

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The present communication brings an account of experiments made to determin the atomic weight of fluorine by a new method. As the work has to be interrupted for a time it was concluded to offer such results as have been obtained.

A record of all previous work on the atomic weight of this element may be found in the third edition of F. W. Clarke's "A Recalculation of the Atomic Weights." Most determinations have been made by changing various fluorides into sulfates. This was the method pursued by Berzelius, Louget, Dumas, De Luca and Moissan, who used the fluorides of calcium, barium, lead, sodium and potassium. Their results vary from 18.85 to 19.14. The chief sources of error in the method are incomplete change of fluoride into sulfate, and loss of material due to the violent escape of hydrofluoric acid. Louget writes that, in spite of all precautions, there was always a slight loss of material. Naturally both these sources of error would lead to high values for the atomic weight.

Christensen[1] treated ammonium manganese fluoride, $(NH_4)_2MnF_5$,

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[1] *J. prakt. Chem.*, [2] 35, 541.