water at 25°, 1.00400; vacuum correction for toluene, +0.00126 g.; vacuum correction for NiCl$_2$, +0.000195 g.

The agreement of the densities found by the two methods is reassuring, not only so far as the specific gravity of the nickelous chloride is concerned, but also because it indicates that no appreciable amount of air is adsorbed upon the surface of the rather finely divided flakes of sublimed salt. Using the specific gravity found by the second method, the volume of the specimen of salt used in the first method is 5.79 cc., which differs from that found experimentally from the weight of air displaced and the density of the air by as much as 0.1 cc. in only one of the three experiments. Since this difference represents less than 0.1 mg. in weight, it is obviously within the limit of error of the experiment.

Summary

The specific gravity of anhydrous nickelous chloride has been found by displacement of air to be 3.52, and by displacement of toluene to be 3.54. The latter value is to be preferred. The experiments also indicate that nickelous chloride does not adsorb appreciable amounts of air.

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THE HYDRATION OF ACETIC AND HYDROCHLORIC ACIDS AND THE FACTORS DETERMINING THE ACTIVITY OF HYDROGEN ION

BY W. C. M. LEWIS, DORIS E. MERRIMAN AND T. MORAN

In a recent paper[1] it was concluded that the activity of chloride ion (and of potassium ion) in solutions of sucrose was completely accounted for by expressing the activity in terms of solvent space, allowance being made for the volume occupied by the sucrose. The present communication deals with the activity of hydrogen ion produced from acetic and hydrochloric acids, respectively, in presence of sucrose and, as will be shown, the analysis is much more complex than that required in the case of the chloride ion.

The Activity of Hydrogen Ion Produced from Acetic Acid

Acetic acid was primarily chosen since, as it is a weak electrolyte, we should expect it to be simpler in its behavior than a strong acid such as hydrochloric acid would be.

The cell of the following composition was fitted up and its e.m.f. determined: N calomel electrode | sat. KCl | N acetic acid; sucrose | H$_2$.

[1] Corran and Lewis, THIS JOURNAL, 44, 1643 (1922).

A saturated solution of potassium chloride was employed to eliminate any potential differences of the boundary liquid, in agreement with the conclusions of Walpole.[2]

It was found that the resistance of solutions of sucrose in N acetic acid was so great as to render impossible any accurate determinations of e.m.f. by the ordinary potentiometer method. Accordingly, the method chosen was that devised by Beans and Oakes.[3] This consists in connecting up in turn the cell whose e.m.f. is required and a standard cell with a condenser, and then discharging the latter through a galvanometer. The ratio of the deflections gives the ratio of the two e.m.f.'s. This is true only when the deflections are practically the same. Accordingly, an e.m.f. (E) of practically the same magnitude as that of Cell A was tapped off from an accumulator by means of a resistance box. The value of E was then determined by means of a potentiometer. The hydrogen-ion activities were calculated from the formula, $\pi_{H+} = 0.2867 + 0.060 \log a_{H+}$, where π_{H+} is the potential difference of the hydrogen electrode, 0.2867 that of the normal hydrogen electrode at 30°, and a_{H+} is the activity of the hydrogen ion.

In calculating π_{H+} from the e.m.f. of Cell A it was assumed that the potential difference of the N calomel electrode at 30° is 0.5682 volt. This is based on the standard value of 0.5600 volt at 18° with a temperature coefficient of 0.00068 volt per degree.[4] The results are shown in Table I. ·

TABLE I

ACTIVITIES AND CONCENTRATIONS OF HYDROGEN ION AT 30°, IN SOLUTIONS OF SUCROSE CONTAINING ACETIC ACID

Conc. of sucrose in moles per liter of solution	Conc. of total water in moles per liter of solution ($M = 18$)	E.m.f. of Cell A in volt	a_{H+}	Relative values of a_{H+}	$C'_{H+(corr.)}$	$C_{H+(corr.)}$
0.000	52.38	0.4208	0.00476	1.00	1.00	1.00
0.292	48.91	0.4176	0.00540	1.13	1.10	1.10
0.585	45.44	0.4144	0.00609	1.28	1.21	1.23
0.877	41.94	0.4111	0.00692	1.45	1.36	1.39
1.169	38.44	0.4088	0.00755	1.59	1.55	1.61
1.460	34.97	0.4037	0.00919	1.93	1.80	1.89
1.755	31.48	0.4014	0.0110	2.30	2.14	2.30

It should be pointed out that the value 0.00476 for the activity of hydrogen ion in N acetic acid agrees well with the e.m.f. determinations of Walpole[2] who worked with 0.25 N acetic acid at 18°. By extrapolating his values to N acid and assuming the potential difference of the normal hydrogen electrode to be proportional to the absolute temperature we find the value 0.00479 for a_{H+} in N acetic acid.

[2] Walpole, *J. Chem. Soc.*, **105**, 2501 (1914).
[3] Beans and Oakes, THIS JOURNAL, **42**, 2116 (1920).
[4] Chroustchoff and Sitnikoff, *Compt. rend.*, **108**, 941 (1889).

Corran and Lewis[1] conclude that chloride ion is soluble in the water of hydration of sucrose. From several points of view hydrogen ion would appear to be insoluble in water of hydration. The most striking evidence in favor of this is found in the values for the activity of hydrogen ion in the presence of potassium and lithium chlorides. Thus in the presence of 3 M potassium chloride the activity of hydrogen ion produced from 0.1 N hydrochloric acid is 0.168, while in the presence of 3 M lithium chloride its value is found to be 0.430.[5] It is generally accepted that lithium chloride is much more hydrated in solution than potassium chloride and, in consequence, these activity values would be in keeping with the fact that hydrogen ion is insoluble in the water of hydration of both salts. Garner and Masson[6] have also come to a similar conclusion, while Wilson,[7] working with sulfuric acid, on the assumption that the increase in the activity of the hydrogen ion is due solely to the hydration of the added salt, has calculated values for the degrees of hydration of various salts. Correcting in this way in the case of the hydrogen-ion activities given above, the hydrogen ion being formed here from acetic acid, and assuming that sucrose is hydrated to the extent of $4H_2O$ per mole,[8] it is found that the acitivity is largely but not completely accounted for. These values denoted by $C'_{H+(corr.)}$ are also shown in Table I.

Two explanations are suggested to account for the divergence of $C'_{(H+ corr.)}$ from a_{H+}. On the basis of increased ionization of the acetic acid on the addition of sucrose (which is essentially the idea of Scatchard[9]) a concentration of hydrogen ion equal to 0.00511 is required in the presence of 1.755 M sucrose to make $C'_{H+(corr.)}$ identical with a_{H+}. It would follow that this amount of sucrose has increased the ionization of the acid by 7.4%, while in solutions containing a concentration of sucrose less than 1.755 M a smaller increase in the dissociation of the acetic acid is found necessary. There is no independent evidence, however, that a sucrose solution is a better ionizing agent than is water itself.

On the other hand existing evidence points to acetic acid being hydrated in solution. Thus Dunstan and Thole,[10] from an examination of the viscosity curves of aqueous solutions of acetic acid at different temperatures, conclude that it is hydrated. Moreover, if we assume that it is hydrated to the extent of 3 monohydrol molecules throughout—the evidence for this assumption is considered later—and then calculate the values of $C_{H+(corr.)}$ on this basis (that is, the concentration of the hydrogen ion, allowing for the space occupied by the sucrose and acetic acid together with

[5] Moran, unpublished results.

[6] Garner and Masson, *Phil. Mag.*, 41, 484 (1921).

[7] Wilson, THIS JOURNAL, 42, 715 (1920).

[8] Moran and Lewis, *J. Chem. Soc.*, 121, 1613 (1922).

[9] Scatchard, *ibid.*, 43, 2402 (1921).

[10] Dunstan and Thole, *J. Chem. Soc.*, 95, 1556 (1909).

their water of hydration), we can account, within the limit of error, for the observed activity values.[11]   The values of $C_{H+(corr.)}$ are recorded in the last 2 columns of Table I.

The Hydration of Acetic Acid

That the acetic acid is hydrated in solution and that the sucrose does not increase the ionization of this acid may be inferred from a series of unpublished results obtained in this Laboratory by Mr. F. P. Stowell. The e.m.f. of the following cell was measured at 25°: N calomel electrode | sat. KCl | 0.1 N HCl and CH_3COOH | H_2, where the acetic acid content was varied from 0 to 2 N. With the value of the normal calomel electrode at 25° (0.5648 volt) known, and by use of the relation $\pi_{H+} = 0.2820 +$ 0.0591 log a_{H+}, where π_{H+} is the potential difference of the hydrogen electrode, the activity of the hydrogen ion in the various hydrochloric-acetic acid mixtures was calculated.

TABLE II

CONCENTRATION OF HYDROGEN ION IN SOLUTIONS OF SUCROSE CONTAINING ACETIC ACID ASSUMING THAT ACETIC ACID IS HYDRATED TO THE EXTENT OF 3

Concentration of HCl=0.1 N

Conc. of acetic acid in moles per liter of solution	Conc. of total water	E.m.f. of cell	a_{H+}	$C_{H+ (corr.)}$
0	55.55	0.3477	0.0794	0.0794
0.10	55.14	0.3474	0.0802	0.0805
0.25	54.82	0.3470	0.0817	0.0815
0.50	53.99	0.3463	0.0840	0.0840
0.75	53.21	0.3454	0.0869	0.0866
1.0	52.52	0.3450	0.0883	0.0891
1.5	50.80	0.3431	0.0951	0.0953
2.0	49.61	0.3419	0.0996	0.1011

[11] The principle of the calculation involved is as follows. Consider first a liter of N acetic acid containing C_{H_2O} moles of total water $(M=18)$ and suppose there are x gram-ions of hydrogen ion produced from the dissociation of the acid. If acetic acid is hydrated to the extent of three, the number of moles of water present as water of hydration is 3 and hence the total number of moles of free water is $C_{H_2O} - 3$. Ascribing unit density to water, the volume of free water is $18(C_{H_2O}-3)$ cc. and, hence, the concentration of hydrogen ion per unit volume of free water is $\dfrac{x}{18(C_{H_2O}-3)}$.

Next, consider a liter of normal acetic acid containing m moles of sucrose and C'_{H_2O} moles of total water. As sucrose is hydrated to the extent of 4, the number of moles of water present as water of hydration is $4m + 3$ and, hence, the concentration of hydrogen ion per unit volume of free water is $\dfrac{x}{18[C'_{H_2O} - (4m + 3)]}$. Thus the relative values of $C_{H+(corr.)}$ in these two cases are 1.00 and $\dfrac{C_{H_2O} - 3}{C_{H_2O} - (4m + 3)}$. It is clear, therefore, that it is unnecessary to know the absolute value of x, as only relative values are considered in the present paper.

If we assume that the total concentration of hydrogen ion present is produced from the hydrochloric acid and that the acetic acid only increases the effective concentration $[C_{H^+(corr.)}]$ of this ion, due to displacement of water, we can account for the values of $C_{H^+(corr.)}$ assuming that the degree of hydration of the acetic acid is 3. Table II gives a summary of the data and results obtained.

It will be observed that on the basis of a hydrate consisting of 3 molecules of water to 1 of acetic acid the hydrogen-ion activities can be satisfactorily accounted for. In view of this it would appear reasonable to eliminate the possibility of sensible increase in ionization of the acetic acid, in the presence of sucrose, and instead to account for the change in activity of the hydrogen ion on the basis of space considerations alone.

In the following section the part played by heat of dilution of the acid in connection with the activity of the hydrogen ion is considered, the presence of a water-displacing agent effectively increasing the concentration of the acid. As will be seen this effect becomes of importance only when a considerable change in hydrogen-ion activity is brought about by the addition of a water-displacing agent. In the case just dealt with, namely, the behavior of hydrochloric acid in the presence of acetic acid, it is justifiable to neglect the possible effect due to the heat of dilution of the hydrochloric acid, since as is shown by the table the total observed change in the activity of the hydrogen ion is small.

On the other hand, when the system, hydrochloric–acid–sucrose, is examined a very great change in the acitivity of the hydrogen ion is observed and, as indicated in the following section, the heat of dilution of the acid has then to be taken into account.

In the case of acetic acid alone in presence of sucrose, we can again neglect the possible heat effect of dilution, as the absolute value of the hydrogen-ion activity (or concentration) is small over the range investigated.

The Activity of Hydrogen Ion Produced from Hydrochloric Acid.— For the examination of hydrochloric acid the following cell was employed: N calomel electrode|sat. KCl| 0.1 N HCl; sucrose|H_2. Preliminary work was carried out which pointed to the fact that the presence of sucrose did not cause the potential difference between the saturated solution of potassium chloride and the 0.1 N hydrochloric acid to be different from the zero value attributed to the junction by Fales and Vosburgh[12] in the absence of sucrose. The e.m.f. of the cell was determined by the ordinary potentiometer method, and the activity of the hydrogen ion at 25° was calculated by means of the formula, $a_{H^+} = 0.2820 + 0.059 \log a_{H^+}$. These activity values are given in the following table.

If, in the present case, we correct the concentration of the hydrogen

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[12] Fales and Vosburgh, THIS JOURNAL, **40**, 1291 (1918).

ion for the space occupied by the sucrose and its water of hydration[18] that is, if we express the concentration of the hydrogen ion in moles per unit

TABLE III

ACTIVITY OF HYDROGEN ION AT 25° AND HEATS OF DILUTION OF HYDROGEN ION FOR 0.1 N SOLUTION OF HYDROCHLORIC ACID IN SUCROSE

Conc. of sucrose in moles per liter of solution	Conc. of total water in moles per liter of solution	a_{H^+}	a_{H^+} (relative values)	$C_{H^+(corr.)}$	$Q_{H^+ cal.}$	$C_{H^+(corr.)} \left[1 + \dfrac{Q_{H^+}}{RT} \right]$
0.000	55.55	0.080	1.00	1.00	0	1.00
0.292	51.95	0.096	1.20	1.10	13	1.12
0.585	48.45	0.115	1.44	1.21	29	1.27
0.877	44.99	0.139	1.74	1.34	45	1.44
1.169	41.62	0.167	2.09	1.50	61	1.66
1.460	38.09	0.200	2.50	1.72	77	1.95
1.755	34.59	0.240	3.00	2.02	93	2.34
2.047	30.94	0.288	3.60	2.44	109	2.89

of free water space, we obtain a series of values of $C_{H^+(corr.)}$ (see Table III, Col. 5) which are very much smaller than the corresponding values of a_{H^+}. In fact, on this basis only about $^2/_3$ of the increase in a_{H^+} on addition of sucrose can be accounted for.

Trevor[14] has shown thermodynamically that the osmotic pressure of a solute is given by the equation

$$PV = Q + \frac{T d(PV)}{dT} \tag{1}$$

where Q is a heat of dilution of the solute defined later (see Eq. 4). In the case of sucrose this is practically zero and, hence, Equation (1) reduces to the well-known form of the gas law,

$$PV = RT, \text{ or } P = RT C_{corr.} \tag{2}$$

where $C_{corr.}$ has been shown by Moran and Lewis[8] to be the concentration of the sucrose after allowing for its own volume together with its water of hydration.

In general, however, Q is not zero. Suppose it to be independent of temperature. Equation 1 then reduces to

$$PV = RT + Q; \text{ or } P = RT C_{corr.} \left(1 + \frac{Q}{RT} \right).$$

Considering the particular case of hydrogen ion, the definition of its activity leads necessarily to the relation, $P = RT a_{H^+}$, whence

$$A_{H^+} = C_{corr.} \left(1 + \frac{Q}{RT} \right) \tag{3}$$

Bancroft[15] has shown that the value of Q in Equation 3 is given by

$$Q = \left(\frac{dQ'}{dC} \right) \times C \tag{4}$$

[18] As the hydrochloric acid itself is only 0.1 N, any water removed as water of hydration of the acid is quite negligible.

[14] Trevor, *J. Phys. Chem.*, 9, 90 (1905).

[15] Bancroft, *ibid.*, 10, 319 (1906).

where C denotes the number of molecular weight of solvent per molecular weight of solute, and where Q' is the heat of dilution of the solute as ordinarily determined by experiment. Richards[16] has determined experimentally the heats of dilution of various salts and acids including hydrochloric acid and potassium chloride. The heat of dilution of hydrochloric acid is made up of two effects, one due to the hydrogen ion and the other due to the chloride ion. MacInnes[17] has given reasons for believing that the activities of potassium and chloride ions are equal, and on the above treatment this would point to the fact that their heats of dilution are necessarily equal.[18] Applying Equation 4 to the case of potassium chloride and employing the result of Corran and Lewis, namely, that both ions are soluble in the water of hydration of sucrose, we obtain values for Q_{KCl}, half of which should be the true heat of dilution of the chloride ion, or $Q_{Cl'}$. Allowing for this in the composite heat values obtained with both hydrogen and chloride ions in the case of hydrochloric acid, we obtain the heats of dilution of hydrogen ion (Q_{H^+}) in solutions of sucrose corresponding to the various concentrations of the sugar employed. Cols. 5, 6 and 7 of Table III give the values thus obtained in the case of 0.1 N HCl-sucrose solutions, assuming that the sucrose merely acts as an inert water-displacing agent.

It is clear that even on allowing for heat of dilution as well as for the space effect, the observed hydrogen-ion activities are not wholly accounted for. This is significant, for it apparently once more brings into prominence the abnormality displayed by a strong electrolyte. However, it must be emphasized that in calculating the heats of dilution the simplest possible mechanism was assumed, namely, that the sucrose played no part whatever in affecting he heats of dilution beyond taking up a certain amount of space and thus concentrating the hydrochloric acid or potassium chloride. It can readily be shown from an analysis of vapor pressures that the presence of sucrose alters the nature of the water by increasing the proportion of monohydrol. In view of this, it might be concluded that sucrose plays a more complex role in affecting the heats of dilution. Unfortunately, direct experimental data on heats of dilution of acids and salts in the presence of sucrose are wanting at the present time. Scatchard[9] has attempted to account for the activity of hydrogen ion (produced from sulfuric acid) in the presence of sucrose, on the basis of molar fractions

[16] Richards, THIS JOURNAL, **43**, 770 (1921).

[17] MacInnes, *ibid.*, **41**, 1086 (1919).

[18] It should be noted that in the paper by Corran and Lewis (Ref. 1) it was *not* found necessary to take into account any factor involving heat of dilution. This is in keeping with the fact that the maximum value of $Q_{Cl'}$ in the range of concentration employed by the above authors is 12.5 calories. In other words, the factor $\left(1 + \dfrac{Q_{Cl'}}{RT}\right)$ is within the range of experimental error.

(which is sensibly the same in the case of sucrose solutions as correcting for solvent space). This did not account completely for the activity, and Scatchard attributed the remainder to increased ionization. His treatment in the present case is obviously inapplicable since, in the case of solutions of sucrose and 0.1 N HCl containing a concentration of 0.877 M or more sucrose, an ionization of much more than 100% would be required. If, however, we employ Scatchard's idea of increased ionization in presence of sucrose, not to account for the whole deviation of the observed a_{H^+} from $C_{H^+(corr.)}$ [where $C_{H^+(corr.)}$ is the concentration calculated on the basis of true solvent space (or molar fractions)], but simply to explain the divergence of $C_{H^+(corr.)}\left[1 + \dfrac{Q_{H^+}}{RT}\right]$ from a_{H^+} as due to change in ionization of the hydrochloric acid, it is found that in the solution containing 2.047 M sucrose, assuming the acid to be completely dissociated, the value of $C_{H^+(corr.)}\left[1 + \dfrac{Q_{H^+}}{RT}\right]$ is 3.61, or practically identical with the value 3.60 for the activity of the hydrogen ion. That is, the discrepancy between observed activity and that calculated on the basis of available space and effect of heat of dilution may be removed by assuming increased ionization of the acid due to the presence of sucrose. As already mentioned, there is no independent evidence for or against this assumption for the case of a strong acid. In the case of acetic acid the evidence is adverse.

The Hydration of Hydrochloric Acid

Fales and Morrell[19] have determined experimentally the velocity of inversion of sucrose and also the activity of the hydrogen ion in the presence of varying concentrations of hydrochloric acid. A mechanism for the inversion process has been suggested by Moran and Lewis[8] according to which the measurable process consists in the interaction of sucrose dihydrate and hydrogen ion represented by the equation $(S, 2H_2O) + H^+ \longrightarrow (S, 2H_2O, H^+)$, where S stands for the sucrose molecule; and the bimolecular velocity constant characteristic of this reaction is given by $k_{bi.} = (k_a \times a_{H_2O}^2 \times \eta^x \times K)/a_{H^+}$, where k_a is the unimolecular velocity constant in terms of activity; a_{H_2O} is the activity of the water; η^x is the viscosity factor for hydrogen ion; K is the equilibrium constant between sucrose dihydrate and sucrose tetrahydrate; and a_{H^+} is the activity of the hydrogen ion. At a given temperature and for a single concentration of sucrose with varying amounts of acid, η^x and K are both constant. Hence, for this case $(k_a \times a_{H_2O}^2)/a_{H^+}$ should be a constant. Fales and Morrell give the values of a_{H^+} and also the observed unimolecular velocity constants. As the concentration of total water present in

[19] Fales and Morrell, THIS JOURNAL, 44, 2071 (1922).

the system for any single experiment and also the degrees of hydration of the sucrose and hydrochloric acid are known, the number of moles of free water can be calculated, from which by employing the relation, $k_a = k_{obs.} \times 0.018 \times$ (conc. of free water), the values of k_a, the unimolecular velocity constants in terms of activity, can be calculated. The remaining factor is $a_{H_2O}^2$, the activity of the water in presence of a constant amount of sucrose and various amounts of hydrochloric acid.

The only available data in this connection are those of H. C. Jones[20] who has measured the freezing-point lowering of various concentrations of hydrochloric acid in water. By considering the vapor-pressure-temperature curves of ice, water and supercooled water, one can obtain the vapor pressures of the various solutions at a series of different temperatures in the region of $0°$, at which temperatures the vapor pressure of water itself is also known. If now we assume that the relative lowering in the vapor pressure (that is, in the activity) is independent of the temperature, we have immediately a measure of the relative activity in presence of various amounts of hydrochloric acid at 35°, taking the vapor pressure of pure water at 35° as unity. In addition, from the data of Berkeley and Hartley[21] it follows that the vapor pressure of a 0.2988 M solution of sucrose is 0.994 that of pure water. The series of relative vapor-pressure values obtained from Jones' data have, therefore, to be reduced by the constant amount 0.006, when the constant amount of sucrose present is 0.2988 mole. The resulting values of a_{H_2O} are given in Col. 6 of Table IV. As already pointed out, the expression $(k_a \times a_{H_2O}^2)/a_{H^+}$ should have a constant value, provided the mechanism suggested by Moran and Lewis is correct.

Sucrose itself is hydrated to the extent of $4H_2O$ per molecule, and it is found that when an average hydration for the hydrochloric acid of $7HO$[22]

TABLE IV

Conc. of Sucrose, 0.2988 mole.   Temperature, 35°.

Conc. of HCl	Moles of free water per liter	$k_{obs.}$ Fales and Morrell	k_a	a_{H^+} Fales and Morrell	a_{H_2O}	$\dfrac{k_a \times a_{H_2O}^2}{a_{H^+}} \times$
1.197	41.13	496×10^{-6}	367×10^{-6}	1.607	0.944	204 [245]
0.8972	43.25	310×10^{-6}	241×10^{-6}	1.124	0.966	200 [229]
0.5981	45.67	187×10^{-3}	154×10^{-6}	0.6887	0.974	212 [231]
0.2990	48.09	837×10^{-7}	724×10^{-7}	0.3334	0.981	209 [218]
0.09964	49.70	252×10^{-7}	225×10^{-7}	0.1102	0.992	201 [204]
9.97×10^{-3}	50.49	237×10^{-8}	215×10^{-8}	0.01233	0.994	172 [172]
9.97×10^{-4}	50.50	221×10^{-9}	201×10^{-9}	0.001134	0.994	175 [175]

[20] Jones, *Carnegie Inst. Pub.*, **60** (1907).

[21] Berkeley and Hartley, *Phil. Trans.*, **218A**, 295 (1919).

[22] Bjerrum [*Medd. K. Vetenskapsakad. Nobelinst.*, **5**, 16, 1–21 (1919)] from freezing-point data calculates that the degree of hydration of HCl lies between 7.5 and 8.5. The lower value 7 (at 35°) obtained in this paper would, therefore, be in good agreement with his value.

per molecule is used, a constant value for $(k_a \times a_{H_2O}^2)/a_{H^+}$ is obtained of approximately 200×10^{-6}. However, in the last two experiments when the concentration of acid is very small, the values of $(k_a \times a_{H_2O}^2)/a_{H^+}$ differ considerably from this number.

If hydrochloric acid were assumed to be unhydrated (a very improbable assumption) the resulting values in the final column would be those in brackets. The assignment of the very reasonable value of 7 to the hydration gives rise to a series of values for the quantity $(k_a \times a_{H_2O}^2)/a_{H^+}$ which are reasonably constant over a wide range of acid concentration as they should be if the above mechanism of inversion is correct. No obvious explanation is presented to account for the divergence observed in the case of very dilute acid solutions. It may reasonably be due to a summation of experimental errors, for the mechanism seems to hold good in the region where the experimental difficulties are not so pronounced. Incidentally, it should be pointed out that the value for $(k_a \times a_{H_2O}^2)/a_{H^+}$ in the presence of 0.292 M sucrose at $35°$ obtained from the data of Moran and Lewis, after making allowance for the difference in units employed by Fales and Morrell, is 202×10^{-6}, or practically identical with the value obtained above.

Summary

1.   The activity of hydrogen ion (produced from acetic acid) in the presence of various amounts of sucrose has been experimentally determined at $30°$.

2.   In the case of acetic acid, the activity of the hydrogen ion can be completely accounted for by assuming acetic acid to be hydrated to the extent of 3 molecules of water for each molecule of acid, and then identifying activity with the concentration of the hydrogen ion per unit of free water space in the sucrose solution.

3.   The change in the activity of hydrogen ion (produced from hydrochloric acid) in the presence of sucrose can not be accounted for by a space correction alone. In this case the heat of dilution of the ion must be considered, and it is shown that by combining the two above factors it is possible to account for 80–90% of the observed activity; no definite conclusion is arrived at as to the causes of the excess activity observed. It is pointed out, however, that the excess might be attributed to an increased ionization of the acid, a modification of an assumption originally made by Scatchard.

4.   The average degree of hydration of hydrogen chloride in solution between 0.1 N and 1.2 N concentration has been calculated by an application of the kinetics of the inversion of sucrose by this acid, employing the data of Fales and Morrell. It is shown to be approximately 7.

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LIVERPOOL, ENGLAND

PHASE RELATIONS IN THE SYSTEM, SODIUM AMIDE-POTASSIUM AMIDE, AS DETERMINED FROM MELTING-POINT CURVES

BY CHARLES A. KRAUS AND EUSTACE J. CUY

Introduction.—Franklin[1] has observed that in liquid ammonia solution sodium amide forms with potassium amide a relatively insoluble compound, the composition of which may be expressed by the formula, $NaNH_2.2KNH_2$. It is not possible to arrive at a conclusion regarding the constitution of this substance without further data as to its properties. It appeared worth while, therefore, to investigate the system, $NaNH_2$–KNH_2, in order to determine what compounds may be separated from the melt, as well as to obtain some information as to the relative stability of the compounds in the fused mixture of the amides.

Experimental Method and Apparatus.—Since the amides react readily with water vapor, carbon dioxide and oxygen,[2] it was found necessary to devise an apparatus for the purpose of preparing the amide mixtures and obtaining their cooling curves in an inert atmosphere.

The alkali metal was weighed in a small steel tube which was fitted with a cap for the purpose of excluding air. After weighing, the metal was introduced into the reaction tube, consisting of a steel cylinder of approximately 37 cm. length and 3.5 cm. diameter, and closed at the top by means of a cap. It was also provided with 2 valves, through one of which ammonia could be introduced and through the other the evolved hydrogen removed and thereafter collected.

After displacing the air in the apparatus by means of ammonia, the bomb was heated in an electric furnace to a temperature in the neighborhood of 300° in an atmosphere of ammonia vapor at a pressure of approximately 10 atmospheres. The higher pressure serves to accelerate the reaction between the metal and the ammonia vapor. The hydrogen formed was collected over water and served as a rough measure of the progress of the reaction. A mercury trap was inserted between the collecting apparatus and the bomb.

The melting point of the amide or of the amide mixture was determined by means of a thermocouple introduced through the cover of the reaction tube. After obtaining a cooling curve with a given mixture, another weighed quantity of metal was added and the process repeated.

Experimental Results.—The results obtained are given in the following table, which will require no further explanation.

[1] Franklin, *J. Phys. Chem.*, **23**, 36 (1919).

[2] De Forcrand, *Compt. rend.*, **121**, 66 (1895).   Drechsel, *Ber.*, **20**, 1456 (1887).