No explanation is offered of the phenomenon of the passivity of air-exposed iron in nitric acid (6 M or less) containing silver nitrate.

Summary

1. The presence of phosphates (except small quantities with aluminum) and of sulfates accelerates the rate of dissolution of iron and aluminum in nitric acid.

2. The presence of phosphate or sulfate modifies the electrical potential difference of passive iron against nitric acid, making the metal more electronegative with respect to the solution.

3. There is no abrupt change with these metals in nitric acid, between the active and the passive states.

4. The effectiveness of anions accelerating dissolution is attributed to the adsorption of these ions at the oxygen film–solution interface.

5. Air-exposed iron is passive in concentrated chromic acid solution. This passivity may be destroyed by reduced pressure, a hydrogen atmosphere, or by wetting with solutions of electrolytes of sufficient concentration.

6. Dilute nitric acid can be made inactive toward air-exposed iron by the addition of silver nitrate.

SEATTLE, WASH. RECEIVED AUGUST 30, 1933

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Accelerated and Retarded Diffusion in Aqueous Solution[1]

BY JAMES W. MCBAIN AND CHARLES R. DAWSON

Graham[2] observed that in a mixture of salts the more rapidly diffusing salt diffuses even more rapidly than when diffusing alone into water. In 1874 Marignac[3] recorded a lengthy table of such data, most of which have not yet been accorded quantitative theoretical treatment, nor have his experiments been repeated. Nernst's fundamental paper[4] rests upon the assumption that the diffusion of ions depends not only upon the concentration gradient but also upon the electrostatic forces which are set up in maintaining the law of electroneutrality when ions possess unequal mobilities. Thus even for a single electrolyte such as hydrochloric acid diffusing into water neither ion can exhibit its proper diffusion coefficient (8.05 for H^+, 1.73 for Cl^-) but instead both ions diffuse at the same rate (2.84 at 25°). Planck's papers[5] constitute a more formal statement of the principles utilized by Nernst.

Arrhenius[6] first applied these principles to mixtures of more than two ions. Many later writers have recorded similar work, usually without reference to the earlier originators.

The present paper brings illustrative data of several striking kinds, using the simplest possible materials, potassium chloride and hydrochloric acid. It further reveals hitherto unsuspected possibilities in the field of diffusion by discovering extremely great acceleration of all the constituents, reacting and non-reacting, in experiments with hydrochloric acid and glycine.

A. Experimental Method

The method of employing constant diffusion columns confined within a porous membrane of sintered glass between two homogeneous bodies of liquid affords one of the simplest, quickest, and yet most precise means of studying diffusion in any field of science. The technique has already been described.[7] The temperature was 25.0°. An important improvement for future work is the use of a symmetrical cylindrical cell divided into two equal compartments by the porous disk and provided at each end with two tubes closed with stopcocks, so that after diffusion columns have been established during the first few hours, fresh solutions of original strength may be placed in each compartment. Solutions were analyzed by means of a Zeiss interferometer supplemented by gravimetric determinations or titrations.

Potassium chloride "Kahlbaum for Analysis" was used, and hydrochloric acid diluted from con-

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(1) Read at the meeting of the Pacific Intersectional Division at Salt Lake City, June 13, 1933.

(2) T. Graham, *Phil. Trans. Roy. Soc.* (London), 805 (1850).

(3) C. Marignac, *Ann. chim. phys.*, [5] **2**, 546 (1874).

(4) W. Nernst, *Z. physik. Chem.*, **2**, 613 (1888).

(5) M. Planck, *Wied. Ann.*, **39**, 161 (1890); **40**, 561 (1890); *Sitzb. preuss. Akad. Wiss.*, p. 285 (1927); p. 9 (1929); p. 367 (1930); p. 113 (1931).

(6) S. Arrhenius, *Z. physik. Chem.*, **10**, 51 (1892).

(7) J. H. Northrop and M. L. Anson, *J. Gen. Physiol.*, **12**, 543 (1929); J. W. McBain and T. H. Liu, THIS JOURNAL, **53**, 59 (1931); M. E. Laing McBain, *ibid.*, **55**, 545 (1933); C. R. Dawson, *ibid.*, **55**, 432 (1933).

stant boiling acid.[8] Glycine from the Eastman Kodak Company was recrystallized three times from conductivity water and salted out with alcohol until the conductivity of the solution showed that the conducting impurities had been removed.

The general equations for the diffusion of the ions in a mixture of hydrochloric acid and potassium chloride may be written

$$D_{\mathrm{H}}G_{\mathrm{H}} = RT\left[G_{\mathrm{H}}U_{\mathrm{H}} - C_{\mathrm{H}}U_{\mathrm{H}}\left(\frac{G_{\mathrm{H}}U_{\mathrm{H}} + G_{\mathrm{K}}U_{\mathrm{K}} - G_{\mathrm{Cl}}U_{\mathrm{Cl}}}{C_{\mathrm{H}}U_{\mathrm{H}} + C_{\mathrm{K}}U_{\mathrm{K}} + C_{\mathrm{Cl}}U_{\mathrm{Cl}}}\right)\right]$$

$$D_{\mathrm{K}}G_{\mathrm{K}} = RT\left[G_{\mathrm{K}}U_{\mathrm{K}} - C_{\mathrm{K}}U_{\mathrm{K}}\left(\frac{G_{\mathrm{H}}U_{\mathrm{H}} + G_{\mathrm{K}}U_{\mathrm{K}} - G_{\mathrm{Cl}}U_{\mathrm{Cl}}}{C_{\mathrm{H}}U_{\mathrm{H}} + C_{\mathrm{K}}U_{\mathrm{K}} + C_{\mathrm{Cl}}U_{\mathrm{Cl}}}\right)\right]$$

$$D_{\mathrm{Cl}}G_{\mathrm{Cl}} = RT\left[G_{\mathrm{Cl}}U_{\mathrm{Cl}} + C_{\mathrm{Cl}}U_{\mathrm{Cl}}\left(\frac{G_{\mathrm{H}}U_{\mathrm{H}} + G_{\mathrm{K}}U_{\mathrm{K}} - G_{\mathrm{Cl}}U_{\mathrm{Cl}}}{C_{\mathrm{H}}U_{\mathrm{H}} + C_{\mathrm{K}}U_{\mathrm{K}} + C_{\mathrm{Cl}}U_{\mathrm{Cl}}}\right)\right]$$

where G is the concentration gradient of the ion represented by the subscript, most conveniently taken as the difference in the concentration of the solutions on the two sides of the membrane, U is the mobility of the ion indicated by the subscript, and D is the diffusion coefficient due to the combined effects of concentration gradient and electrostatic potential gradient. If D is expressed in cm.^{2}/day and U in terms of ionic conductivity, then RT at 25° is replaced by $RT \times 86400/96500^2 = 0.02300$.

At times zero, these equations are equivalent to those first derived by Arrhenius[6] and used for particular cases by later authors, and to those recently published by Hartley and Robinson[9] and by Bruins.[10] They may be expressed in more general form using the notation of Planck. For positive ions at 25°

$$D'G' = 0.02300\,\{G'u' - n'c'u'\,(U_{\mathrm{G}} - V_{\mathrm{G}})/(U + V)\}$$

and for negative ions

$$\bar{D}'\bar{G}' = 0.02300\,\{\bar{G}'v' + n'\bar{c}'v'\,(U_{\mathrm{G}} - V_{\mathrm{G}})/(U + V)\}$$

where u', u'', are the equivalent conductances of positive ions
v', v'', are the equivalent conductances of negative ions
n', n'', are the valences of positive ions
$\bar{n}'$, $\bar{n}''$, are the valences of negative ions
c', c'', are the concentrations of positive ions
$\bar{c}'$, $\bar{c}''$, are the concentrations of negative ions
G', G'', the concentration gradient of positive ions
$\bar{G}'$, $\bar{G}''$, the concentration gradient of negative ions
D', $\bar{D}'$, are the observed diffusion coefficients in cm.^{2}/day

$$U_{\mathrm{G}} = n'u'G' + n''u''G'' +$$
$$V_{\mathrm{G}} = \bar{n}'v'\bar{G}' + \bar{n}''v''\bar{G}'' +$$
$$U = n'u'c' + n''u''c'' +$$
$$V = \bar{n}'v'\bar{c}' + \bar{n}''v''\bar{c}'' +$$

Such equations apply directly to steady state diffusion in a membrane of constant properties but, like Nernst's original equation, they are strictly valid only for infinitely dilute solution.

In practice the diffusion columns are not constant throughout the twenty-hour duration of the experiment, but this is allowed for by using the equation of McBain and Liu[7] or else, with an inaccuracy of less than one per cent., by taking the concentration gradient G equal to the arithmetic mean of the original and final concentration gradients, that is, the original concentration difference minus the change of concentration on either side of the membrane during the experiment.

B. Systems Containing Hydrochloric Acid and Potassium Chloride

Three distinct types of experiment were carried out in which hydrochloric acid diffused with, through, and against potassium chloride. Each experiment was performed in triplicate, a typical example being given in detail in Table I, the mean

TABLE I

DATA FOR THE DIFFUSION OF H^+, K^- AND Cl^- IONS, SHOWING THE INITIAL (I) AND FINAL (F) DIFFERENCES IN CONCENTRATION ON THE TWO SIDES OF THE MEMBRANE, AND THE RESPECTIVE DIFFUSION COEFFICIENTS FOR KCl DIFFUSING WITH HCl INTO WATER

H^+		K^-		Cl^-				
I	F	I	F	I	F	D_{I}	D_{K}	D_{Cl}
0.0315	0.0181	0.099	0.085	0.131	0.103	4.82	1.30	2.05
.0314	.0186	.099	.086	.131	.105	4.78	1.29	2.04
.0313	.0168	.099	.083	.130	.100	4.85	1.29	2.05

TABLE II

EXPERIMENTAL AND CALCULATED DATA FOR THE DIFFUSION OF H^+, K^+, AND Cl^- IONS[a]

G_{H}	G_{K}	G_{Cl}	D_{H} Calcd.	D_{H} Obs.	D_{K} Calcd.	D_{K} Obs.	D_{Cl} Calcd.	D_{Cl} Obs.
KCl diffusing with HCl into water								
0.0957	0.0942	0.190	4.07	3.55	0.95	1.06	2.51	2.36
.0795	.0945	.176	4.30	3.65	0.99	1.10	2.47	2.26
.0248	.0917	.117	5.58	4.82	1.27	1.30	2.28	2.08
.0085	.0095	.0190	4.14	3.69	1.08	1.19	2.41	2.44
.525	.0752	.597	3.05	2.83	0.76	0.80	2.77	2.73
.0087	.2025	.211	7.30	6.50	1.58	1.55	1.83	1.72
HCl diffusing in KCl, the KCl being originally of uniform concentration throughout the system								
0.0825	0.0055	0.0872	4.45	4.61	−1.05	−1.17	3.56	3.04
HCl against KCl, the solutions being originally on opposite sides of the membrane								
0.0822	0.0872	0.006	4.30	4.40	2.42	2.50	−1.10	−1.13

[a] The values calculated from the Nernst formula for the separate ions at infinite dilution are D_{H} 8.05, D_{K} 1.70, D_{Cl} 1.73, D_{HCl} 2.84, D_{KCl} 1.71.

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(8) G. A. Hulett and W. D. Bonner, THIS JOURNAL, **31**, 390 (1909).

(9) G. S. Hartley and C. Robinson, *Proc. Roy. Soc.* (London), **134A**, 20 (1931).

(10) H. R. Bruins, *Kolloid-Z.*, **57**, 158 (1931); **59**, 263 (1932).

results being collected in Table II and, for the particular case of $N/10$ solutions, in Table III.

TABLE III

DIFFUSION OF $N/10$ HCl WITH, AGAINST, AND THROUGH $N/10$ KCl

	D_{H^+}	D_{K^+}	D_{Cl^-}
With	3.67	1.11	2.27
Against	4.40	2.51	(−1.13)
Through	4.62	(−1.17)	3.04

In scrutinizing Tables II and III, it should be remembered that diffusion of $N/10$ KCl into water is 1.63 and that of $N/10$ HCl is 2.71, so that the movement of the hydrogen ion is much accelerated in all cases. In the first line of Table III this is at the expense of the potassium ion, which is retarded, the chlorine ion adopting an intermediate value. In the second line, the chlorine was originally of uniform concentration throughout but both it and the potassium ion move so as to compensate for the acceleration of the hydrogen ion so that here the potassium ion is accelerated. In the third line the hydrogen ion is to a certain extent set free to tend toward the intrinsic velocity which it would possess if unhampered by electrical influences and moved solely by concentration gradient.

The values for the chlorine ion in the second row of Table III and for potassium ion in the last row of Table III are put in brackets because they are calculated upon the basis of a diffusion gradient of decinormal, whereas in fact there was initially no concentration gradient whatsoever for these ions as they were the same on both sides of the membrane. They then moved against the concentration gradient which they were creating, and hence are marked with a minus sign in the tables.

It is evident from Table II that the observed and calculated results are in all cases in substantial agreement to within at least 10% for K^+ and Cl^- and 20% for H^+. Distinct deviations should be expected from the fact that the equations were those holding accurately only for infinite dilution and any association of ions or formation of undissociated molecules would lower the diffusion coefficients.

A second factor which would affect especially the more concentrated solutions is the phenomenon pointed out in previous communications;[11] that is, the collision effect exerted by diffusing columns upon all molecules in their path, driving them along and producing an effect somewhat similar to that of the Langmuir diffusion pump for gases. Graham obtained the effect in one of his experiments but ascribed it to an experimental error amounting to one-eighth of the diffusion coefficient he was measuring. It was noted again by Thovert[12] in 1914 without his finding an explanation, and also by Osborne[13] in 1914, but explained away by Walpole[14] in the following year as being due to the Arrhenius effect which we have already discussed, Walpole having overlooked the fact that some of the data referred to non-electrolytes. This collision factor is important in concentrated solutions and has to be taken into account wherever simultaneous diffusions are occurring in either the same or opposite directions. To conclude, in all solutions the actual diffusion rate of an ion is accelerated or retarded by the other ionic species present in the solution and is also distinctly influenced by any diffusion columns whether of electrolytes or of non-electrolytes.

C. Extreme Acceleration of Diffusion

Lastly, we would present some examples of accelerated diffusion of a magnitude hitherto not thought possible. They have been obtained in experiments with hydrochloric acid and amino acetic acid.

The diffusion of glycine is of interest in itself, in that glycine is the simplest relation of the proteins, with an isoelectric point at a PH 6.1, where it is only very slightly dissociated, both dissociation constants being well known. The experiments were of four types, those in which glycine diffused into water of the same PH, those in which glycine plus hydrochloric acid diffused into hydrochloric acid of the same PH, those in which glycine plus hydrochloric acid diffused into water, and those in which glycine and hydrochloric acid diffused against each other. In the last case even the non-reacting component, chlorine ion, yielded a remarkable speed of movement from one side of the porous membrane to the other.

The diffusion coefficient of glycine itself (into water) is almost constant in the lower concentrations but, although it is practically undissociated, its molecules are too small to apply the Sutherland–Stokes–Einstein equation.

In the second set of experiments the diffusion

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[11] See especially J. W. McBain and T. H. Liu, Ref. 7.

[12] J. Thovert, *Ann. phys.*, **2**, 407 (1914).

[13] W. A. Osborne and L. C. Jackson, *Biochem. J.*, **8**, 246 (1914).

[14] G. S. Walpole, *Biochem. J.*, **9**, 132 (1915).

TABLE IV

THE DIFFUSION OF GLYCINE

A. Diffusion of glycine P_H 6.1 into water

Concn. of glycine	1.05 *N*		0.1 *N*		0.01 *N*	
D	0.745	0.745	0.889	0.894	0.905	0.905
	.750		.898		.915	
	.740		.895		.895	

B. Diffusion of *N*/10 glycine and HCl into HCl of same P_H

P_H	5.24	5.08	4.20	3.14	2.80	1.55
D	0.895	0.930	1.045	1.015	1.095	1.003

C. Diffusion of glycine and HCl into water

Concentration		Concn. from P_H			
HCl	Glycine	H^+ before	H^+ after	D_G	D_{Cl}
0.106	0.108	0.0258	0.0055	0.80	1.79
.313	.104	.21	.028	.57	2.43
.995	.095	.68	.138	.58	2.76

D. Diffusion of *N*/10 glycine into HCl, the latter simultaneously diffusing into the glycine

Concn. HCl	Concn. H^+ in glycine after diffusion		D_G		D_{Cl}
0.0014	0.000005	1.05	1.04	7.27	7.3
		1.04		7.40	
				7.30	
.006			1.02		6.9
.012	.00009		1.06		6.5
.024	.0002		1.17		5.7
.026	.0002		1.23		5.75
.0526	.0005		1.18		4.08
.1	.008	1.20	1.18	3.59	3.59
		1.18		3.61	
		1.16		3.57	
.252	.002		1.61		3.45
.52	.01	1.78	1.82	3.19	3.19
		1.85		3.20	
		1.84		3.17	
1.03	.04		2.24		3.14
2.06	.24		1.92		2.82

recorded was that of the glycine, partly as molecules or zwitter ions and partly as glycine cations; all three may be assumed to possess nearly the same mobility. If so, the Nernst equation for infinite dilution would predict a diffusion coefficient of 1.19 for glycine hydrochloride, could it exist by itself without excess of hydrochloric acid. The free hydrochloric acid present throughout has two opposing effects, one through transformation of more glycine into glycine ion, the other through the effect of any electrolyte added at uniform concentrations throughout, in enabling each diffusing ion to move more independently at a rate more nearly corresponding to its intrinsic mobility. The importance of these factors in influencing the diffusion of all charged colloids will be illustrated in another communication dealing with egg albumin.

The third set of experiments illustrates the principles already discussed in the experiments in which a mixture of potassium chloride and hydrochloric acid diffused into water, since here the excess of hydrochloric acid was so large that most of the glycine was converted to hydrochloride. Hence the glycine ion, like the potassium ion, is retarded and the chlorine ion accelerated. The intrinsic mobility of chlorine ion in decinormal solution is the same as that of potassium chloride since both ions are alike, namely, 1.63.

In the last set of experiments where decinormal glycine diffused against solutions of hydrochloric acid and the resulting solutions were analyzed for glycine chloride (as AgCl), the essential difference between these and all other experiments here recorded is that chemical reaction between hydrogen ion and glycine accompanied the diffusion. The chlorine ion was, of course, left unchanged. Nevertheless in very dilute solution it moves with as much as five times its normal velocity or true diffusion coefficient. Similarly, the glycine in some of the experiments is moving with as much as three times its normal rate of diffusion. The fastest diffusion of chlorine ion ever before observed was that in hydrochloric acid at infinite dilution, 2.84, whereas in our table only one value falls so low and others rise as high as 7.3.

It is evident that facts such as these which are now so readily observed and subjected to quantitative study are of great importance in studying the mechanism of reactions in biological systems and living organisms where it now becomes apparent that the rate of transfer of material may be many times as rapid as would be predicted from standard diffusion data secured in solutions in which no chemical reaction is occurring.

Finally, it may be mentioned that the diffusion coefficients of 1.03 *N* glycine diffusing against 0.0125 *N* HCl are D_G 0.785 and D_{Cl} 4.7, as compared with D_G 1.04 and D_{Cl} 7.3 for 0.1 *N* glycine diffusing against 0.0014 *N* HCl. The great decrease in observed diffusion coefficients with increased concentration may best be explained by the hypothesis of "collision with the molecules of a diffusing column" previously mentioned.

Summary

1. Attention is called to the simple principles due to Nernst, first elaborated by Arrhenius in 1892, which govern the acceleration or retardation of all ions in the presence of other ionic species

whether diffusing with or against them or present in uniform concentration throughout. These are illustrated by varied experiments with potassium chloride and hydrochloric acid. The general equations (for infinite dilution) are stated and shown to be common to the cases studied by all writers since Arrhenius. Collision effects of diffusing columns modify the results at higher concentrations.

2. Unprecedentedly high rates of diffusion were found for all constituents in experiments where glycine diffused against hydrochloric acid. In the case of chlorine ion in dilute solution, this amounted to as much as a five-fold increase, although the chlorine ion was not reacting.

STANFORD UNIVERSITY, CALIF.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Crystal Structure of NdAl

BY CHARLES W. STILLWELL* AND ELMER E. JUKKOLA

Because of the scarcity of x-ray data for the alloys of the rare earth metals it has been impossible to consider this group in any of the recent attempts to systematize, on the basis of their structure, binary alloys and intermetallic compounds in general. Any information is of value, therefore, which may indicate how alloys of these elements fit into the general scheme, particularly as to whether or not they resemble the better known alloys of other transition elements.

Experimental Part

The first preparation of NdAl was incidental to the preparation of metallic neodymium by the decomposition of neodymium amalgam in an alundum crucible.[1] The brittle, metallic, octahedral crystals formed were found to contain 85–88% neodymium, indicating the compound NdAl (84.4% Nd) with a varying amount of excess neodymium, probably in solid solution. Other specimens were prepared by fusing together the theoretical amounts of the two metals.

The analysis of an average set of diffraction data for the alloy is shown in Table I, appended to which are other data needed for the structure analysis. The diffraction data were obtained by reflecting CuK radiation from the sharp edge of a multicrystalline piece of the metal. The camera employed has been described before.[2] The method is useful to avoid the necessity for powdering, and to permit the protection of the surface of substances easily oxidized. It is accurate to within 0.5%.

TABLE I

DIFFRACTION DATA FOR THE COMPOUND NdAl

Intensity	d_{hkl}	hkl	a_0
m	3.73	100	3.73
s	2.64	110	3.74
s	2.16	111	3.74
s	1.866	200	3.73
s	1.667	210	3.73
vs	1.522	211	3.73
s	1.318	220	3.73
s	1.237	221, 300	3.71
s	1.176	310	3.72
s	1.122	311	3.73
m	1.075	222	3.73
w	1.032	320	3.72
vs	0.997	321	3.73
vw	.932	400	3.73
s	.907	410, 322	3.74
s	.880	411, 330	3.73
vw	.857	331	3.73
m	.834	420	3.73
w	.818	421	3.74
m	.797	332	3.74

Average $a_0 = 3.73 \pm 0.01$ Å.

Molecular weight of NdAl (84.4% Nd) = 171
Analysis of specimen from which above pattern was obtained = 86.5% Nd
Molecular weight of this specimen = 199
Pycnometric density of this specimen = 6.05 at 25°
Number of molecules NdAl per unit cell = 0.97

Discussion

The diffraction data indicate a cesium chloride type of structure. Since the diffracting powers of neodymium and aluminum are so different, it is to be expected that planes containing only aluminum atoms may not produce diffraction lines, and it is the neodymium atoms, lying on a simple cubic lattice, which produce the pattern obtained. Assuming this structure, the body

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[1] Jukkola, Audrieth and Hopkins, to be published soon.

[2] Stillwell and Robinson, THIS JOURNAL, **55**, 127 (1933).