on long standing in direct sunlight. This phenomenon will also be investigated.

Summary.

(1) Previous investigations have involved too limited a range of concentrations to elucidate the nature of chromate solutions.

(2) Hydrolytic equilibrium-changes involve color-changes; hydration-equilibria, though less important, also cause color-changes; ionization-equilibria, except as involving hydrolysis or hydration, probably have no effect on color-changes.

(3) Heat has marked effects on colors.

(4) Varied quantities of acids and alkalies have very important effects on the colors of chromates.

(5) Very dilute solutions of all chromates (CrO_3, H_2CrO_4, $H_2Cr_2O_7$, $H_2Cr_3O_{10}$, $H_2Cr_4O_{13}$) contain only chromate molecules or ions.

(6) More concentrated solutions contain both H_2CrO_4 and $H_2Cr_2O_7$ molecules and ions; chromate solutions contain dichromates and *vice versa.*

(7) At still greater concentrations or in acid solutions or when heated, dichromates contain trichromates and, probably at still greater concentrations, trichromates contain tetrachromates.

(8) Below the chromate-dichromate transition concentration, hydrated forms of chromate exist and probably produce color-variations.

SEATTLE, WASH.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE IDEAL DIFFUSION COEFFICIENT AND A FUNDAMENTAL LAW CONCERNING THE DIFFUSION OF DISSOLVED SUBSTANCES IN LIQUIDS.

BY GEORGE MCP. SMITH.

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Introduction.

The significance of the diffusion coefficient *D* is derived from the formula,

$$dS = -Dq\frac{dc}{dx}dt,$$

in which *dS* is the quantity of the dissolved substance which passes at the point *x* in the time *dt* through the cross-section *q* of a diffusion cylinder under the influence of the concentration-fall *dc*/*dx*. The value of *D* depends upon the temperature and upon the actual concentration.

If we consider an ideal diffusion cylinder of unit cross-section, 1 cm.^{2}, in which the concentration difference 1 exists in the solution between two horizontal planes 1 centimeter apart, and in which the solution in the plane half-way between these has the concentration *c*, then the concentration of the solution in the lower plane is $c + {}^1/_2$, and that of the solution in the upper plane is $c - {}^1/_2$. The diffusion upwards, then, is caused by the existence of a concentration-fall of unity in the unit distance. If dc/dx in the above formula is equal to 1 gram per centimeter, then dS will be expressed in grams; or, if dc/dx is equal to 1 mol per centimeter, dS then will be expressed in mols. In both cases the numerical values of dS will be identical. A simple definition of D is as follows:

The diffusion coefficient D is the quantity of the dissolved substance, in grams, which passes in unit time, *e. g.*, 1 day, in the unit cross-section, 1 cm.^{2}, through the unit concentration-fall, 1 g., with unit velocity, 1 cm. per day.[1]

If, now, in a table of diffusion coefficients, determined at a given temperature with dilute solutions of substances which do not iônize or present other complications, we divide each D-value by the molecular weight of the substance in question, we obtain a set of *special* diffusion coefficients, D/M, which may be defined as the *number of mols* of the dissolved substance which in the unit cross-section pass in unit time through the *concentration-fall of one gram* with unit velocity.

Identical numerical values of D/M can, of course, be derived from the diffusion coefficients when dc in the above equation is expressed in terms of molal concentration. In that case, D is the number of mols of the dissolved substance that diffuse in unit time through unit area under the influence of a concentration-fall of one mol in unit distance; and, as has already been pointed out, the numerical values are identical with those of D as defined above.

But the question at once arises as to the physical significance of the values obtained by dividing these numbers, which are already expressed in mols, by the molecular weights of the respective compounds.

Here the values of D/M may be regarded as obtained in each case by dividing the weight of D mols of an ideal compound of unit molecular weight by the molecular weight of the respective compound.

The significance of the values thus obtained is as follows: If, *in each case*, the molecules of the ideal compound be regarded as possessing the same size and configuration and the same mean free-path velocity as those of the real compound, then they would encounter the same resistance that the latter do in their progressive forward movement; but the momentum of each such imaginary molecule of unit molecular weight would be equal only to the reciprocal value of that of a molecule of the real compound. That is to say, that only D/M mols of the imaginary substance would diffuse through unit distance in the time that it takes for D mols of the compound to do the same thing.

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[1] This is simply an expression in English of the value of dS in the above formula when q = 1 cm.^{2}, dc = 1 gram, dx = 1 cm., and dt = 1 day.

Viewed in this light, the values of D/M assume a real physical significance, *and we obtain in them a common denominator, the ideal diffusion coefficient,*[1] *to which the ordinary diffusion coefficients of different substances may be reduced,* provided that the molecules of the substances do not ionize or engage in other disturbing complications.

The IDEAL DIFFUSION COEFFICIENT, $D/M = I$, *indicates the number of mols of a compound which in the unit cross-section would pass in unit time through the unit molal concentration-interval with unit velocity, provided that each molecule of the compound—while retaining its size, configuration, and free-path velocity—had its momentum reduced to the reciprocal value.*

A. The Ideal Diffusion Coefficient and the Diffusion of Dissolved Substances in Water.

L. W. Öholm, who has carried on most of his work with aqueous solutions, has determined numerous diffusion coefficients at comparable temperatures and, in the case of almost every individual substance, at different concentrations; he has investigated the diffusion of many electrolytes,[2] and also that of many non-electrolytic organic compounds[3] with molecular weights varying all the way from 59 to 504. His results in the latter case are particularly valuable, since without them much necessary data would not be available at the present time.

TABLE I.[4]

	Substance.	Equivalent concentration.	Diffusion coefficient. D.	Molecular weight. M.	Ideal diffusion coefficient. 10^4. I.	Log M.	Log 10^4. I.
1.	Acetamide......	0.25	0.900	59	152.5	1.77085	2.18339
2.	Urea...........	0.25	1.022	60	170.3	1.77815	2.23130
3.	Dicyandiamide..	0.2	0.895	84	106.5	1.92428	2.02754
4.	Glycerol........	0.25	0.705	92	76.6	1.96379	1.88440
5.	Hydrochinone...	0.25	0.665	110	60.5	2.04139	1.78143
6.	Resorcinol......	0.25	0.652	110	59.3	2.04139	1.77286
7.	Saligenin.......	0.25	0.619	124	49.9	2.09342	1.69827
8.	Penta-erythrite..	0.2	0.589	136	43.3	2.13354	1.63658
9.	Alloxan.........	0.25	0.563	142	39.6	2.15229	1.59822
10.	Mannite........	0.25	0.485	182	26.6	2.26007	1.42567
11.	Ecgonine.......	0.1	0.604	185	32.6	2.26717	1.51387
12.	Caffeine........	0.05	0.488	194	25.2	2.28780	1.40062
13.	Salicin..........	0.12	0.402	286	14.1	2.45637	1.14786
14.	Cane sugar......	0.25	0.369	342	10.8	2.53403	1.03300
15.	Milk sugar......	0.2	0.361	342	10.6	2.53403	1.02348
16.	Raffinose.......	0.25	0.297	504	5.9	2.70243	0.77033

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[1] Owing to the importance of this new unit of diffusion, the writer would suggest the use of the capital letter I as its symbol.

[2] *Z. physik. Chem.*, 50, 309–49 (1904–05).

[3] *Ibid.*, 70, 378–407 (1910); *Chem. Zentr.*, **1913**, I, p. 1649 f.

[4] The D values in the table are taken from the work of L. W. Öholm, *Z. physik. Chem.*, **70**, 401 (1910), and *Chem. Zentr.*, **1913**, I, p. 1649. In this table water of crystallization was not taken into consideration.

If now, in the cases of substances of varying molecular weights, such as those listed in Table I, we plot the values of the ideal diffusion coefficients as ordinates and those of the molecular weights as abscissas, we obtain the curve shown in Fig. 1.

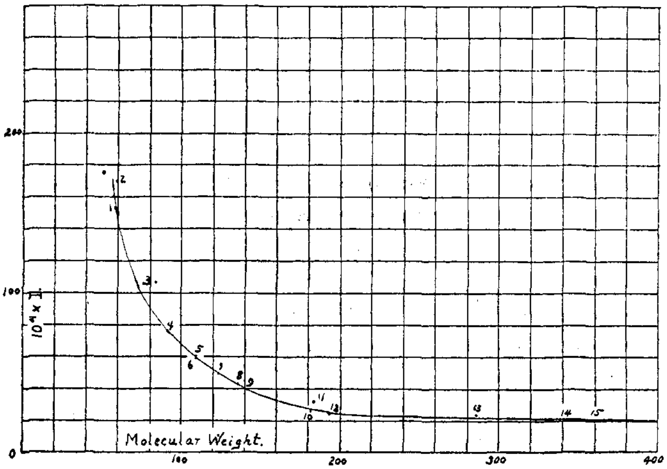

Figure 1

From the appearance of this curve it occurred to the writer also to plot the logarithms of these values, and upon doing so the straight line BC shown in Fig. 2 was obtained.

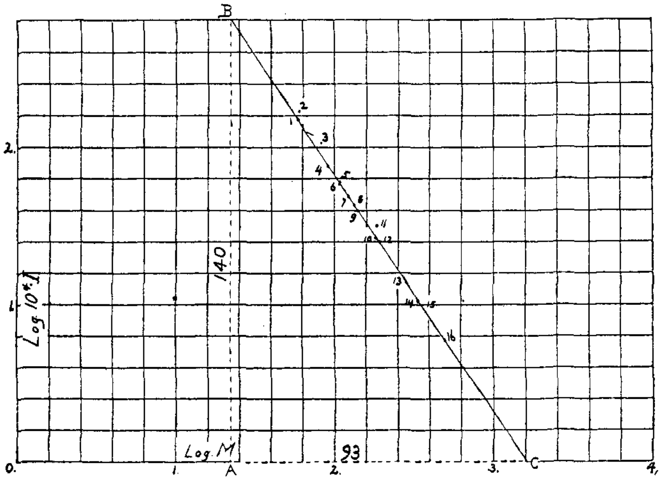

Figure 2.

As the graph of the straight line BC, in Fig. 2, we have the equation:

$$\log I + n \log M = \log K,$$

Table II.[1]

	Substance.	c.	$D_{20°}$.	M.	Log M.	$10^4 \times I$.	Log I.	Log IM^n.	K.
1.	Acetamide	0.25	0.900	59	1.77085	152.5	—2.18339	0.84922	*7.07*
2.	Urea	0.25	1.022	60	1.77815	170.3	—2.23130	0.90812	8.09
3.	Dicyandiamide	0.2	0.895	84	1.92428	106.5	—2.02754	0.92435	8.40
4.	Glycerol	0.25	0.705	92	1.96379	76.6	—3.88440	0.84068	*6.93*
5.	Hydrochinone	0.25	0.665	110	2.04139	60.5	—3.78143	0.85453	*7.15*
6.	Resorcinol	0.25	0.652	110	2.04139	59.3	—3.77286	0.84596	*7.02*
7.	Saligenin	0.25	0.619	124	2.09342	49.9	—3.69827	0.84970	*7.07*
8.	Penta-erythrite	0.2	0.589	136	2.13354	43.3	—3.63658	0.84841	*7.05*
9.	Arabinose	0.25	0.552	150	2.17609	36.8	—3.56585	0.84173	*6.95*
10.	Nicotine	0.1	0.456	162	2.20952	28.1	—3.44944	0.77565	5.97
11.	Mannite	0.25	0.485	182	2.26007	26.6	—3.42567	0.82797	6.73
12.	Ecgonine	0.1	0.604	185	2.26717	32.6	—3.51387	0.92686	8.45
13.	Alloxan (4 H_2O)	0.25	0.563	214	2.33041	26.3	—3.42010	0.92829	8.48
	Alloxan (anhydrous)	0.25	0.563	142	2.15229	39.6	—2.59822	0.83827	*6.89*
14.	Caffeine (1 H_2O)	0.05	0.488	230	2.36173	21.2	—3.32669	0.88203	7.62
	Caffeine (anhydrous)	0.05	0.488	212	2.32634	23.0	—3.36208	0.86415	7.31
15.	Salicin	0.12	0.402	286	2.45637	14.1	—3.14786	0.84567	*7.01*
16.	Cane sugar	0.25	0.369	342	2.53403	10.8	—3.03300	0.84772	*7.04*
17.	Maltose (1 H_2O)	0.25	0.348	360	2.55630	9.67	—4.98528	0.83353	*6.82*
	Maltose (anhydrous)	0.25	0.348	342	2.53403	10.2	—3.00755	0.82227	6.64
18.	Milk sugar (1 H_2O)	0.2	0.361	360	2.55630	10.0	—3.00121	0.84946	*7.07*
	Milk sugar (anhydrous)	0.2	0.361	342	2.53403	10.8	—3.02348	0.83820	6.89
19.	Raffinose (5 H_2O)	0.25	0.297	594	2.77379	5.00	—4.69895	0.87461	7.49
	Raffinose (anhydrous)	0.25	0.297	504	2.70243	5.89	—4.77033	0.83856	*6.90*

Mean of the 13 values in italics = 7.00

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[1] In the case of compounds containing water of crystallization, two values of K are calculated; the values of D expressed in mols are the same in either case.

in which K is a constant and n is the slope of the line BC. *From this there is obtained a new fundamental law of diffusion, which is expressed by the formula,*

$$I\,M^n = K,$$

from which, if the values of n and K have been determined for a given set of conditions, the corresponding value of I in the case of any substance of known molecular weight, and therefore the theoretical value of D, may be calculated; or, if, in the case of a given substance, the value of D has been determined experimentally, then the molecular weight of the substance may be calculated. We have the formulae:

$$I = K/M^n; \quad D = IM; \quad M = (K/D)^{1/n-1}.$$

In the case of the hydrodiffusion of non-electrolytes in dilute solution at 20°, we obtain from Fig. 2 for the slope of the line BC the value,

$$n = AB/AC = 140/93 = 1.5054.$$

The values of K for this case are given in Table II.

In his first paper on the hydrodiffusion of the non-electrolytes, Öholm[1] plots the values of D at 20° for different concentrations, and, by continuing the curves to the Y-axis, he obtains the values at infinite dilution; from these values of D he derives four of the values of $D\sqrt{M}$ given in Table III. His values for M, however, are those of the compound without its water of crystallization, and to the writer it would appear unjustifiable to leave this entirely out of consideration. For that reason three more values have been added in italics.

The approximate relation, $D\sqrt{M}$ = const., has been derived[2] from Graham's law for the *effusion* of gases through narrow openings in thin solid partitions; the law does not hold strictly, even in the case of gases, for *diffusion*.

TABLE III.[3]

	A.			B.				
	D_∞ 20°.	$\sqrt{M}$.	$D\sqrt{M}$.	$t°$.	c.	D.	M.	$D\sqrt{M}$.
Cane sugar	0.382	18.5	7.067	11.0	0.25	0.282	342	5.2
Milk sugar	0.377	18.5	6.975	....	....	....	...	...
Milk sugar + H_2O	*0 377*	*18.97*	*7.151*	....	....	....	...	...
Maltose	0.373	18.5	6.901	10.2	0.25	0.280	342	5.2
Maltose + H_2O	*0.373*	*18.97*	*7.076*	*10.2*	*0.25*	*0.280*	360	*5.3*
Raffinose	0.316	22.45	7.096	10.8	0.25	0.230	504	5.2
Raffinose + $5H_2O$	*0.316*	*24.37*	*7.701*	*10.8*	*0.25*	*0.230*	594	*5.6*

Öholm[4] has determined the values of D_∞ at 20° for dextrin, arabinose,

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[1] *Z. physik. Chem.*, 70, 400–404.

[2] Cf. F. Exner, *Pogg. Ann.*, 155, 457 f (1875); G. Hüfner, *Wied. Ann.*, 60, 134 (1896); H. Euler, *Ibid.*, 63, 273 (1897).

[3] Öholm does not calculate the values of $D\sqrt{M}$ for the diffusion data at 10°; these are given, however, under B of this table.

[4] *Z. physik. Chem.*, 70, 400 f.

and nicotine, in addition to those for the four sugars listed in Table III. He also has determined the corresponding values in the cases of the substances investigated in his second paper; but, since his values are not included in the abstract of his paper,[1] they have been redetermined by the writer according to Öholm's method. The method is shown in Fig. 3,

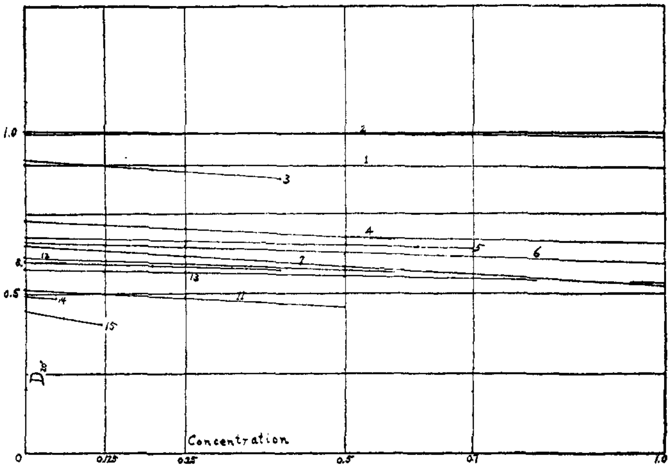

Figure 3.

and the numerical results are given in Table IV, together with Öholm's values for the seven substances referred to above.

The values of log M and of log $10^4\,I$ in Table IV are plotted in Fig. 4[1] and from these we get the relation,

$$n = AB/AC = 140/94 = 1.4894.$$

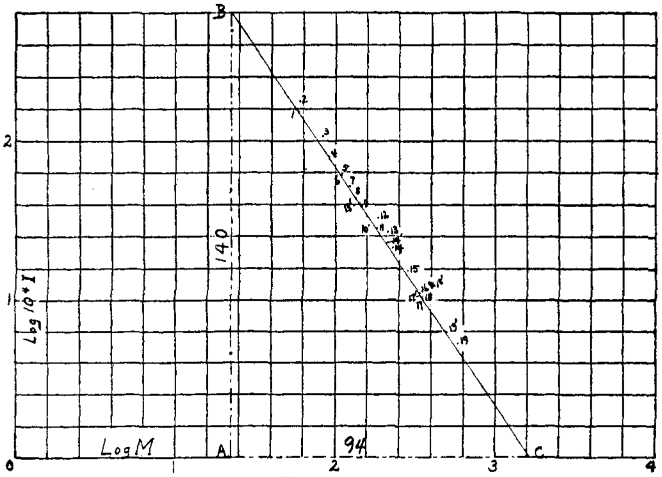

Figure 4.

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[1] *Chem. Zentr.*, **1913**, I, 1649.

TABLE IV.[1]—DIFFUSION DATA AT 20° FOR INFINITE DILUTION.

	Substance.	D_∞.	M.	Log M.	$10^4 \times I$.	Log I.	Log IM^n.	K.
1.	Acetamide	0.902	59	1.77085	152.9	—2.18436	0.82184	*6.64*
2.	Urea	1.070	60	1.77815	178.3	—2.25123	0.89960	[7.93]
3.	Dicyandiamide	0.920	84	1.92428	109.5	—2.03951	0.90551	[8.04]
4.	Glycerol	0.730	92	1.96379	79.3	—3.89953	0.82438	*6.67*
5.	Hydrochinone	0.678	110	2.04139	61.6	—3.78984	0.83027	*6.76*
6.	Resorcinol	0.660	110	2.04139	60.0	—3.77815	0.81858	*6.59*
7.	Saligenin	0.650	124	2.09342	52.4	—3.71949	0.83741	*6.88*
8.	Penta-erythrite	0.600	136	2.13354	44.1	—3.64461	0.82229	*6.64*
9.	Arabinose	0.582	150	2.17609	38.8	—3.58883	0.82988	*6.76*
10.	Nicotine	0.476	162	2.20952	29.4	—3.46809	0.75893	[5.74]
11.	Mannite	0.511	182	2.26007	28.1	—3.44835	0.81448	*6.52*
12.	Ecgonine	0.612	185	2.26717	33.1	—3.51958	0.89628	[7.87]
13.	Alloxan (4 H_2O)	0.575	214	2.33041	26.9	—3.42926	0.90016	7.95
13'.	Alloxan (anhydrous)	0.575	*142*	2.15229	*40.5*	—3.60738	0.81299	*6.50*
14.	Caffeine (1 H_2O)	0.490	230	2.36173	21.3	—3.32847	0.84611	[7.01]
14'.	Caffeine (anhydrous)	0.490	*212*	2.32634	*23.1*	—3.36386	0.83870	[6.90]
15.	Salicin	0.445	286	2.45637	15.6	—3.19199	0.85048	[7.25]
16.	Cane sugar	0.382	342	2.53403	11.2	—3.04803	0.82220	*6.64*
17.	Maltose (1 H_2O)	0.373	360	2.55630	10.4	—3.01541	0.82275	*6.65*
17'.	Maltose (anhydrous)	0.373	*342*	2.53403	*10.9*	—3.03768	0.81185	6.48
18.	Milk sugar (1 H_2O)	0.377	360	2.55630	10.5	—3.02004	0.82738	*6.72*
18'.	Milk sugar (anhydrous)	0.377	*342*	2.53403	*11.0*	—3.04231	0.81648	6.55
19.	Raffinose (5 H_2O)	0.316	594	2.77379	5.32	—4.72590	0.75716	5.72
19'.	Raffinose (anhydrous)	0.316	*504*	2.70243	*6.27*	—4.79726	0.82225	*6.64*
20.	Dextrin	0.103	172x					

Mean of the 13 values in italics. K = 6.66

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[1] The numbers in Fig. 3 correspond to those of the compounds listed in this table. n = 1.4894.

Making use of the empirical formula, $D\infty \times \sqrt{M} = 7$, at 20°, Öholm[1] obtains for the molecular weight of dextrin the numerical value 4440, from which x in the formula $(C_6H_{10}O_5)_x$ assumes the value 27.3.

Upon employing the formula given above, we obtain for M the value,

$$M = (K/D)^{1/n-1} = (6.66/0.105)^{2.0433} = 4815;$$

and for x the value,

$$x = 4815/162 = 29.72.$$

Öholm[2] assigns to dextrin the formula $(C_6H_{10}O_5)_{27\pm1}$; in the light of the above calculation, the formula would be $(C_6H_{10}O_5)_{30}$, of which the theoretical molecular weight is 4860.

Upon comparing the data in Tables II and IV, it will be seen that in each table there are six substances that behave abnormally. Five of these are common to both tables, namely urea, dicyandiamide, nicotine, ecgonine, and caffeine.[3] Salicin,[3] which is normal in Table II, behaves abnormally in Table IV; and mannite does the opposite, though it is almost normal in Table II.

Of the substances that are known with water of crystallization, caffeine is abnormal. But in both tables maltose and milk sugar give values of K which are closer to the mean if we derive the value of M from the hydrated compounds. On the other hand, alloxan and raffinose, which crystallize with 4 and 5 molecules of water, respectively, give normal values of K only if we derive the value of M from the anhydrous compounds. The behavior of these substances would seem to depend upon the relative stability of their hydrates at 20°; the explanation may lie in the existence of an equilibrium between the hydrate on the one hand and the anhydrous compound and water on the other.

By plotting the logarithms of M and I, in the case of Öholm's data[4] at about 10°, the value of n in the formula $IM^n = K$ was found to be 1.4286 for 0.25 molal solutions. Then by substituting this value for n in the formula $M = (K/D)^{(1/n-1)}$, the value of K (= 3.354) having been determined by calculation for anhydrous raffinose, the molecular weights of the other substances have been calculated. The results are given in Table V.

TABLE V.

	$t°$.	c.	D.	K.	$(K/D)^{1/n-1}$.	Theoretical value. M.
Arabinose	9.4	0.25	0.388	...	153	150
Cane sugar	11.0	0.25	0.282	...	323	342
Maltose (1 H_2O)	10.0	0.25	0.272	...	351	360
Raffinose	10.9	0.25	0.233	3.354	...	...

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[1] *Z. physik. Chem.*, 70, 404 f.

[2] *Ibid.*, p. 405.

[3] A possible explanation for the abnormal behavior of caffeine, and of salicin in this case, is offered in a footnote on p. 858.

[4] *Z. physik. Chem.*, 70, p. 393 ff.

B. The Ideal Diffusion Coefficient and the Diffusion of Gases through Water.

According to the well-known law of Graham, the *effusion* velocities of two gases vary inversely as the square roots of their densities. This law was later extended by Exner[1] also to the passage of gases through absorbent liquids, and according to him the volumes of two gases that pass through the liquid film in a given time roughly vary directly as their absorption coefficients and inversely as the square roots of their densities.

Exner studied the passage of gases through very thin soap-bubble membranes only; but later, G. Hüfner[2] studied the phenomenon in the case of thicker layers of liquid. He succeeded in overcoming the difficulties which arose from convection currents in the thicker layers by placing the water upon a thin plate of *hydrophane*—a porous mineral which absorbs water, but through which water does not pass except under appreciable pressure—and allowing the diffusing gas to enter from below or above as the case might require.

The process just referred to differs essentially from effusion and from diffusion in the narrower sense in that the water of the partition is capable of absorbing the gases, so that it takes the gas in at one side and gives it out at the other. It is conditioned, not only by the state of motion of the gaseous substance but also by the movements of the molecules of the liquid partition; and especially by the fact that the gaseous molecules have to penetrate the surface film of the liquid, both upon entering and upon leaving the latter.

In Hüfner's experiments with oxygen, for example, the lower part of the vertically disposed diffusion tube contained moist oxygen; above this there was situated the hydrophane plate, covered with a column of water 1 or 2 cm. high and about 0.75 cm. in diameter, through which the gas was allowed to diffuse upwards. The upper surface of the water was kept in contact with fresh nitrogen gas, which, saturated with moisture, was very slowly passed through this part of the diffusion tube.[3]

In slowly diffusing upwards through the column of water, under these

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[1] *Pogg. Ann.*, **155**, 321, 443 (1875).

[2] *Wied. Ann.*, 60, 134–68 (1896); *Z. physik. Chem.*, **27**, 227–49 (1898).

[3] For detailed particulars in regard to the experimental work, the reader is referred to the original papers of Hüfner. It may be stated, however, that allowance was made in the calculation for the resistance of the hydrophane plate; *e. g.*, in the case of carbon dioxide, 0.4202 cc. (calc. for 760 mm.) passed through the plate and a 0.5 cm. layer of water in 1 day at 16.4°, and 0.2105 cc. passed through the plate and a 2.0 cm. layer of water in the same time at 16.3°. Then, assuming that the diffusing gas-volumes vary inversely as the thickness of the (water) layers penetrated, $0.4202\ (w + 0.5) = 0.2105\ (w + 2.0)$, whence $w = 1.005$ cm.; *i. e.*, in order to pass through the moist hydrophane plate 0.05 cm. thick, carbon dioxide requires the same time as it would under like conditions require to pass through a layer of water with the same cross-section but 1.005 cm. thick.

conditions, the oxygen gas is supposed to keep the lowest layer of the water saturated with itself; the uppermost layer of the water, however, always contains only a relatively insignificant quantity of dissolved oxygen, since by means of the current of nitrogen the partial pressure of the former gas above the surface of the water is kept practically at zero.

Now, if the water column were 1 cm. thick and its cross-sectional area equal to 1 cm^2., and if the partial pressure of the oxygen gas below it were kept equal to 1 atm., then in the lowest layer of the liquid there would be maintained a concentration of dissolved oxygen equal to α cc. of the gas per cc. of solution, α being the absorption coefficient of oxygen for water at the temperature of the experiment—*e. g.*, 0.030 at 21.7°. That is to say, the concentration difference between the top and bottom layers of the liquid would be equal to 0.030 cc.; and if, under these conditions, 0.048535 cc. of oxygen diffused through the column of water in 1 day, then $0.048535 \div 0.030 = 1.62$ cc.[1] would have diffused through in the same time, had the concentration difference between the two layers been kept equal to 1 cc., or 1.62 mols would have done the same had the concentration difference been maintained at 1 mol per cm. In other words, 1.62 is the diffusion coefficient of oxygen *through* water, at 21.7°.

As a matter of fact, it is possible that the lowest layer of the liquid is never completely saturated with the gas, under the above conditions, and it is difficult to believe that the concentration of the dissolved gas in the uppermost layer of the water is equal to zero. This assumption presupposes that the dissolved gas molecules are able to leave the upper layer of the water without encountering any more resistance than they meet in their upward passage through the liquid; while in reality they do have to break through the dense surface film of the water in order to escape into the gaseous space above. In this respect the values of the diffusion coefficients of gases *through* water, as determined by Hüfner, would seem to be not strictly comparable with the values obtained for the diffusion of dissolved substances *in* water; they are, however, certainly comparable among themselves.

The experimental results of Hüfner are given in Table VI, and in Fig. 5 are plotted the logarithms of the ideal diffusion coefficients and those of the molecular weights of the gases. The corresponding values at infinite dilution for acetamide, one of the substances of normal behavior in Table IV, are also plotted, in order to show what position the curve in Fig. 4 would assume in relation to that for the gases now being considered. The value of n in this case is,

$$n = 140/192 = 1.5326.$$

---

[1] Hüfner himself designates this as 1.62 cm., evidently meaning that 1 cc. of the gas would pass through 1.62 cm. of water per cm^2. of surface, under a concentration difference of 1 cc. per cm. distance.

TABLE VI.[1]

	Gas.	$t°$.	D.	$D\sqrt{M}$.	$I \times 10^2$.	Log M.	Log $10^2 I$.	$IM^n = K$.
1.	Hydrogen......	16.	7.53	10.6	376.5	0.30103	2.57576	10.8
2.	Hydrogen......	21.	4.45	...	222.5	0.30103	2.34733	...
3.	Hydrogen......	16.	4.09	...	204.5	0.30103	2.31069	...
4.	Ammonia......	20.0	1.260	5.2	7.41	1.23045	0.86992	5.5
5.	Nitrogen.......	21.7	1.73	9.2	6.17	1.44747	0.79058	9.8
6.	Oxygen........	21.7	1.62	9.2	5.06	1.50515	0.70437	9.9
7.	Nitrous oxide..	16.2	1.35	9.0	3.07	1.64365	0.48668	9.7
8.	Carbon dioxide.	16.4	1.37	9.1	3.11	1.64345	0.49327	9.9
9.	Chlorine.......	16.3	1.098	9.3	1.55	1.85077	0.18983	10.1
10.	*Acetamide......*	*20.0*	*0.902*	*(6.93)*	*1.529*	*1.77085*	*0.18436*	*(6.64)*

When we consider the experimental difficulties encountered by Hüfner in determining such small quantities of gas as those which actually diffused through the water in his apparatus, the appearance of the curve in Fig. 5 is striking, to say the least; it is very near, and practically parallel to that obtained in Fig. 4, and, in spite of the probable justness of the considerations advanced on p. 857, together with the effect of the counter diffusion of another gas, the gases nevertheless appear to diffuse faster than the theory would require. The cause of this may partially lie in the extremely low concentration of the solutions with which the experiments in the case of the gases were actually performed.[2]

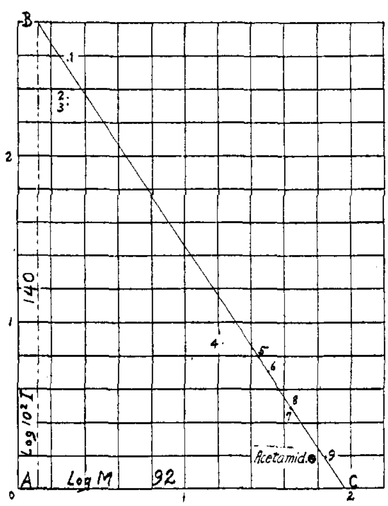

Figure 5.

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[1] Hüfner obtained the first value for hydrogen by means of the capillary method of Stefan; the gas entered, but did not leave the water. Hüfner himself does not consider the value exact. The second and third values were obtained by the hydrophane method, the former with the counter diffusion of air, the latter with that of carbon dioxide. This fact, together with the difference in temperature, might well account for the different figures. However, the absorption coefficient of hydrogen for water is so small that the latter values are probably farther removed from the truth than the first.

The value for ammonia was obtained by the diffusion of ammonia gas into water in a diffusion cylinder so arranged that the gas entered from above, while fresh running water was kept in contact with the lower surface of the hydrophane plate, the vertical arm of the diffusion tube which held the plate being immersed in the water.

The value for chlorine was obtained by means of Stefan's capillary method.

[2] The molal concentration of saturated solutions of the gases at the temperatures of the experiments and at 760 mm. have maximum values as follows: $H_2 = 0.0008$, $N_2 = 0.0007$, $O_2 = 0.0014$, $N_2O = 0.033$, $CO_2 = 0.043$, and $Cl_2 = 0.11$. It will be noted in Fig. 3 that D for caffeine, which diffused too fast, was actually determined

It will be noted in the table that the values for ammonia are very abnormal; Hüfner[1] was unable to account for this in a satisfactory manner. He does mention that Scheffer[2] found for ammonia at 4.5° a diffusion coefficient of 1.06—a higher value than he himself found at 13° (1.052). The reason for this is really not far to seek; the absorption coefficient of ammonia is 760 at 13°, *i. e.*, 1 cc. of water at this temperature will dissolve 0.57 gram of ammonia gas, giving about 1.75 cc. of solution. Such a solution is nearly 20 times normal! Neither were Scheffer's solutions dilute; they were about 0.6 and 3.0 normal, respectively.[3]

C. The Ideal Diffusion Coefficient and the Diffusion of Metals in Mercury.

M. von Wogau[4] has carried out an extensive investigation on the diffusion of metals in mercury, and it was in this connection that the writer, some years ago, published a paper,[5] of which the present one may be regarded as a continuation.

Although at that time it had been shown that the crystalline amalgams of the alkali and alkali earth metals are chemical compounds of the respective metals with mercury, von Wogau, in the discussion of his experimental results, assumed that these metals existed in mercurial solution in the form of monatomic molecules. It has since been shown by the writer[6] that even in dilute mercurial solution the metals in question exist in the form of compounds of the general formula $MeHg_n$, containing only one atom of the alkali or alkali earth metal to the molecule. And, taking the mass law into consideration, it would indeed be a surprising fact if the compounds in question did dissociate to a marked degree upon the addition of a large excess of mercury.[7]

If, however, granting for the time being the assumption of von Wogau, we plot the logarithms of the resulting ideal diffusion coefficients of the metals listed in Table VII with those of their molecular (*i. e.*, atomic) weights, we obtain the points shown in Fig. 6.

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only at 0.05 molal concentration. Also salicin, which in Table II, at 0.12 molal concentration, has normal values, was also determined at 0.07 molal concentration, and the value at infinite dilution obtained from these values gave to it an abnormal value. No other substances in Table IV were measured at concentrations below 0.1 molal.

[1] *Z. physik. Chem.*, **27**, 236.

[2] *Ibid.*, **2**, 390 (1888).

[3] Cf. note to Table VI.

[4] *Ann. Physik*, [4] **23**, 345–70 (1907).

[5] *Ibid.*, [4] **25**, 252 (1908); *Z. anorg. Chem.*, **58**, 381 (1908).

[6] *Z. anorg. Chem.*, **58**, 381 (1908). A summary of the literature concerning the crystalline compounds may be found in this paper.

[7] Heycock and Neville, *J. Chem. Soc.*, **55**, 671 (1889), actually do suppose that a compound is formed upon the addition of sodium to mercury, which, upon the further addition of sodium, dissociates into sodium and monatomic mercury molecules.

TABLE VII.

	Amalgam.	Number of separate determinations.	Average temperature. $t°$.	Average concentration. %.	Mean value. D.	Exner's rule. $D\sqrt{A}$.	Atomic weight. M.	Log M.	Log $10^8 I$.
1.	Lithium......	3	8.2	0.141	0.66	1.75	6.94	0.84136	1.97818
2.	Sodium......	4	9.6	0.140	0.64	3.07	23.00	1.36173	1.44445
3.	Potassium....	5	10.5	0.119	0.53	3.32	39.10	1.59218	1.13210
4.	Calcium.....	2	10.2	0.1	0.54	3.42	40.07	1.60282	1.12957
5.	Zinc.........	6	11.5	0.1033	2.18	17.63	65.37	1.81538	1.52308
5′.	Zinc.........	3	*99.2*	0.112	*2.90*	*23.5*	65.37	1.81538	1.64702
6.	Rubidium....	3	7.3	0.157	0.46	4.25	85.45	1.93171	0.73105
7.	Strontium....	5	9.4	0.144	0.47	4.40	87.63	1.94265	0.72955
8.	Cadmium....	3	8.7	0.128	1.45	15.37	112.40	2.05077	1.11060
8′.	Cadmium....	3	*99.1*	0.130	*2.96*	*31.4*	112.40	2.05077	1.42052
9.	Tin..........	4	10.7	0.145	1.53	16.7	119.0	2.07555	1.10914
10.	Caesium.....	4	7.3	0.1475	0.45	5.19	132.81	2.12323	0.52998
11.	Barium......	3	7.8	0.093	0.52	6.10	137.37	2.13789	0.57811
12.	Thallium.....	4	11.5	0.144	0.87	12.43	204.0	2.30963	0.62989
13.	Lead........	3	9.4	0.138	1.50	21.6	207.1	2.31618	0.85991
13′.	Lead........	2	*99.2*	0.138	*1.92*	*27.6*	207.1	2.31618	0.96712

In this case also von Wogau tests Exner's rule that $D\sqrt{M}$ = const., assuming as the values of M the atomic weights of the respective metals. He finds the values that are listed in Table VII under the heading $D\sqrt{A}$, and which are far from being constant.

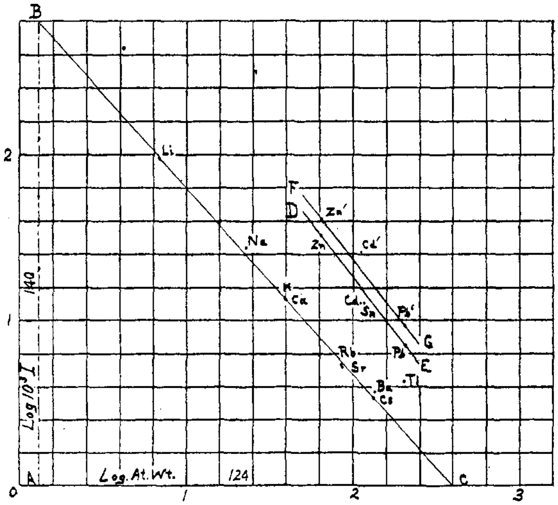

Figure 6.

Long before this, Ostwald[1] had expressed the view that—in harmony with the relationship, $D\sqrt{M}$ = const., as established by Hüfner[2] and Euler[2] for the diffusion of non-electrolytes in aqueous solution — the analogous relationship would be found to obtain for the diffusion of metals in mercurial solution; namely, that $D\sqrt{A}$ = const. G. Meyer,[3] on the other hand, pointed out that this was improbable, since the mean free-path l of the metallic atoms is proportional to the product $D\sqrt{A}$; and,

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[1] *Z. physik. Chem.*, **24**, 530 (1897).

[2] *Loc. cit.*

[3] *Wied. Ann.*, **64**, 752 (1898).

if the latter were constant, then the atoms of all metals would have equal mean free-paths.[1]

Turning now to Fig. 6, we note that the alkali and alkali earth metals all give values that fall on, or very near to, the line *BC*, while zinc and lead, which are known to be incapable of combination with mercury,[2] at about 10° fall on the line *DE*, and at 99° on the line *FG*, which is parallel to *DE*.

Thallium, which with mercury forms the compound $TlHg_2$,[3] gives a value that lies between the lines *BC* and *DE;* and as to cadmium and tin, which fall near the line *DE*, both Bijl[3] and Puschin,[3] and also Würschmidt,[4] conclude from their work that these metals are incapable of entering into combination with mercury. Van Heterin,[5] on the other hand, believes that he has found indications that tin may combine with mercury; he could not, however, derive a formula for the supposed compound.

TABLE VIII.[6]

	Dissolved substance.	Average concentration. Mols per liter.	*D*.	$D\sqrt{M}$.	*M*.	Log *M*.	Log *I*.	$IM^n = K$.
1.	Zn	0.214	2.18	17.6	65.37	1.81538	—2.52308	14.8
2.	Cd	0.154	1.45	15.4	112.4	2.05077	—2.11060	12.6
3.	Sn	0.165	1.53	16.7	119.0	2.07555	—2.10914	13.7
4.	Pb	0.0902	1.50	21.6	207.1	2.31618	—3.85991	17.3
5.	$AuHg_2$	....	0.72	17.6	598.4	2.77699	—3.08034	13.5
6.	$TlHg_2$	0.0322	0.87	21.4	605.2	2.78190	—3.15762	16.1
7.	$LiHg_3$	0.0314	0.66	16.3	608.7	2.78440	—3.03514	12.5
8.	$NaHg_5$	0.0185	0.64	20.5	1026.	3.01115	—4.79503	16.4
9.	$CaHg_5$	0.0130	0.54	17.4	1043.	3.01828	—4.71411	13.0
10.	KHg_6	0.0130	0.53	18.7	1243.	3.09447	—4.62981	13.9
11.	$RbHg_6$	0.0165	0.46	16.5	1289.	3.11025	—4.55251	12.3
12.	$SrHg_6$	0.0151	0.47	16.9	1291.	3.11093	—4.56117	12.5
13.	$CsHg_6$	0.0149	0.45	16.4	1336.	3.12581	—4.52750	12.2
14.	$BaHg_6$	0.0094	0.52	19.0	1341.	3.12743	—4.58857	14.1

Mean value: K = 13.9

By taking as a basis what is known in regard to the compounds formed by mercury with other metals, the writer has succeeded in arriving at the

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[1] Riecke's molecular diffusion theory (*Z. physik. Chem.*, **6**, 504 (1890)) furnishes the formula: $l = 0.01332 \times 10^{-8} \times \sqrt{1 + 0.00367t} \times D\sqrt{M}$.

[2] H. C. Bijl, *Z. physik. Chem.*, **41**, 641 (1902); N. Puschin, *Z. anorg. Chem.*, **36**, 201–254 (1903); J. Würschmidt, *J. Chem. Soc.*, **104**, II, 101.

[3] N. S. Kurnakow and N. Puschin, *Z. anorg. Chem.*, **30**, 86 (1902).

[4] *Loc. cit.*

[5] *Z. anorg. Chem.*, **42**, 129 (1904).

[6] The value for gold, D = 0.72, at 11°, was determined by Roberts-Austen, *Proc. Royal Soc.*, **59**, 283 (1896).

The average molal concentrations of the amalgams were obtained on the assumption that the specific gravity of the dilute amalgams at about 10° is equal to that of mercury at 20° (*i. e.*, 1 liter = 13.546 kg.); this assumption is not far from the truth.

data given in Table VIII.[1] It will be noted that Exner's rule, that $D\sqrt{M}$ = const., roughly holds also in this case.

Plotting, now, the values of log M and of log $10^4 I$, we obtain the points shown in Fig. 7. They all lie on, or very near to, the line BC, and lead, which is known to be incapable of combining with mercury, occupies the position that is farthest removed from the line. For n we obtain in this case the value

$$n = AB/AC = 140/96 = 1.4583.$$

Substituting the value of n in the equation $IM^n = K$, we arrive at the values of K which are given in the last column of the table. The mean value derived from these is $K = 13.9$.

Assuming now that 13.9 is the correct value of K, the theoretical values of D can be calculated by means of the formula

$$D = K/M^{(n-1)} = 13.9/M^{0.4583.}$$

These values are given in Table IX, together with those actually obtained by von Wogau.

TABLE IX.[2]

	Dissolved substance.	Mean experimental value with probable error assigned by von Wogau.	Calculated D-value.	Nearest result from a single experiment.	Difference.
1.	Zn.............	2.18 ± 0.16	2.047	2.04	—0.007
2.	Cd.............	1.45 ± 0.09	1.596	1.53	—0.066
3.	Sn.............	1.53 ± 0.064	1.555	1.50	—0.055
4.	Pb.............	1.50 ± 0.09	1.207	1.48	+0.273
5.	$AuHg_2$..........	0.72 (Roberts-Austen)	0.744	....	....
6.	$TlHg_2$..........	0.87 ± 0.076	0.738	0.81	+0.072
7.	$LiHg_3$..........	0.66 ± 0.045	0.736	0.72	—0.016
8.	$NaHg_5$..........	0.64 ± 0.017	0.579	0.63	+0.051
9.	$CaHg_5$..........	0.54 ± 0.022	0.575	0.56	—0.015
10.	KHg_6..........	0.53 ± 0.032	0.526	0.51	—0.016
11.	$RbHg_6$..........	0.46 ± 0.007	0.522	0.46	—0.062
12.	$SrHg_6$..........	0.47 ± 0.035	0.521	0.53	+0.009
13.	$CsHg_6$..........	0.45 ± 0.017	0.513	0.47	—0.043
14.	$BaHg_6$..........	0.52 ± 0.014	0.513	0.52	+0.007

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[1] Concerning the constitution of the liquid amalgams of the alkali and alkali earth metals, see G. McP. Smith, *Z. anorg. Chem.*, **58**, 381 (1908); and, in regard to the compounds $LiHg_3$ and $NaHg_5$ at ordinary temperatures, see G. McP. Smith and H. C. Bennett, THIS JOURNAL, **32**, 622 (1910), and *Z. anorg. Chem.*, **74**, 172 (1911).

[2] Gold being heavier than mercury was caused by Roberts-Austen to diffuse upwards. But, since all the other metals are specifically lighter than mercury (Pb = 11.3, Tl = 11.8), von Wogau was forced to measure their diffusion downwards. Accordingly, by means of a very ingenious arrangement of horizontally sliding plate-glass plates, each of which contained a single circular perforation, he gently slid the small disc of the amalgam (which filled the perforation of the upper plate) over the column of mercury which was contained in the concentric perforations of the lower plates. At the end of the experiment he separated the different sections of the mercurial solution by the same means, for analysis.

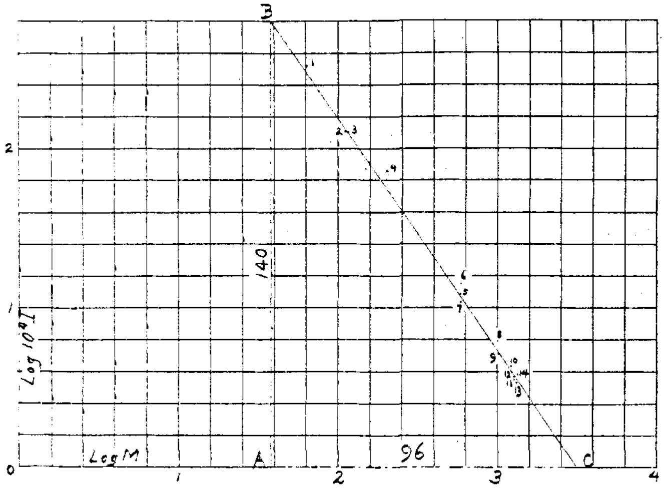

Figure 7.

The calculated values agree, on the whole, very well with those obtained by experiment.

D. The Equation $IM^n = K$, and Its Analogy to the Equation, pv^ν = const., for the Polytropic Expansion of Gases.

The values of n in the equation $IM^n = K$, in the cases discussed above, are given in Table X.

TABLE X.

Table.	Case.	Concentration.	Temperature.	n.
2.	Hydrodiffusion of organic compounds..	0.25	20°	1.5054
4.	Hydrodiffusion of organic compounds..	Infinitely dilute	20°	1.4894
5.	Hydrodiffusion of organic compounds..	0.25	10°	1.4286
6.	Hydrodiffusion of gases..............	*Very* dilute	16°–20°	1.5326
8.	Diffusion in mercurial solution........	*Very* dilute	About 10°	1.4583

It is now easy to explain Exner's rule, that $D\sqrt{M}$ = const., in terms of the above equation. Since in that equation $I = D/M$, we have,

$$IM^n = DM^{(n-1)} = K;$$

it will be seen in the table that in every case the value of $(n - 1)$ roughly approximates 0.5, whence we arrive at the rough approximation

$$D\sqrt{M} \doteqdot \text{const.}$$

The equation $IM^n = K$, which was derived in this form simply to facilitate the processes of calculation, may of course be converted into the form

$$MI^\nu = C,$$

in which $\nu = 1/n$ and C is a constant. In this form, the analogy that exists between this equation and that for the polytropic expansion of a gas—pv^ν = const.—will readily be recognized. Both equations are those of processes, and, in deriving the equation $MI^{\nu} = C$, we have analyzed the process of diffusion, which itself is one of expansion, into two components: one of these, I, corresponds to v, and the other, M, to p, in the equation $pv^{\nu} = \text{const.}$

In conclusion, it may be stated that, upon applying the ideas involved in the conception of the ideal diffusion coefficient to the hydrodiffusion of electrolytes, and to the diffusion of gases into one another, the writer has succeeded in arriving at certain regularities; these, however, it is desired to further investigate, before publication. In connection with the diffusion of gases, an experimental investigation is also planned, since the right kind of data appear to be lacking in this case.

THE UNIVERSITY OF ILLINOIS,
URBANA, ILL.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 98.]

SOLUTIONS OF METALS IN NON-METALLIC SOLVENTS. V. THE ELECTROMOTIVE FORCE OF CONCENTRATION CELLS OF SOLUTIONS OF SODIUM IN LIQUID AMMONIA AND THE RELATIVE SPEED OF THE IONS IN THESE SOLUTIONS.[1]

BY CHARLES A. KRAUS.

Received March 11, 1914.

Introduction.

It was shown in the fourth paper of this series that the conduction process in solutions of the metals in ammonia is an ionic one. The positive carrier is identical with the positive ion of the salts of the same metal, while the negative carrier, which appears to be the same for different metals, can consist only of the negative electron e^-, either free or in association with ammonia. The characteristic properties of the metal solutions are due to the presence of the negative carrier.

With nonsoluble electrodes, such as platinum, the negative carrier passes into and out of the solution without observable material effects. That portion of the current which is carried through the solution by the negative carrier is, therefore, similar to the current in a metal, and in passing a current from a solution of one concentration to a solution of another concentration the only work involved is that of transferring the positive carrier.[2]

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[1] Previous papers of this series have appeared as follows: "I," THIS JOURNAL, 29, 1557 (1907); "II," *Ibid.*, 30, 653 (1908); "III," *Ibid.*, 30, 1197 (1908); "IV," *Ibid.*, 30, 1323 (1908). The sentence beginning on line 25, p. 1332 of the fourth paper should read: "According to this hypothesis, the negative carrier should move more *slowly* in dilute than in concentrated solutions, ..."

[2] This is true for very dilute and very concentrated solutions. At intermediate concentrations the influence of the solvent envelope must be taken into account, as will be described below.