Chemistry. — "The influence of pressure on the velocity of diffusion of metals in mercury." By Prof. ERNST COHEN and Dr. H. R. BRUINS.

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1. Nothing has been known up to the present on the subject of the effect of pressure on the velocity of diffusion of a substance in a liquid. 1)

More accurate information as to this effect is not only very desirable in connection with certain geological problems, but also for the solution of definite questions in molecular theory. According to EINSTEIN the following equation holds:

$$D = \frac{RT}{N} B,$$

where D denotes the diffusion-coefficient of a solute, R the gasconstant, T the absolute temperature of the experiment, N AVAGADRO'S number, and B the mobility of the solute (i.e. the distance which a molecule covers in unit time in its movement through the liquid, when unit force acts on it).

Hence diffusion measurements offer a direct method for determining the mobility of the molecule. This quantity depends on the molecular forces, which are mutually operative between the molecules; it changes, therefore, according as the condition of the medium, in which the diffusion takes place, is changed. The simplest change which the medium can experience is evidently a compression; the distance between the molecules becomes then smaller, whilst the kinetic energy remains unaltered. Viewed from this standpoint, an investigation of the influence of pressure on the diffusion constant must be looked upon as of special interest.

¹) In their communication on the subject of the effect of high pressure on the properties of solid substances [Zeitschr f. anorg. Chemie 80, 281 (1913)] JOHNSTON and ADAMS make this statement: "Some investigations have been carried out in this laboratory on the influence of uniform pressure on the velocity of diffusion (solid substances in solid substances). They indicate that uniform pressure increases the velocity of diffusion: but it would be premature to consider this as established, and it is scarcely allowable to draw the conclusion that uniform pressure actually must have such an effect".

2. The limitations are so numerous which the experimental difficulties impose on us in our choice of a suitable system, when undertaking accurate measurements of diffusion at high pressures, that actually only a narrow choice of possibilities remains. We have first to think of a system such that we may be in a position to follow from outside, by electrical or optical methods, the progress of the diffusion which is taking place inside a pressure apparatus.

One might imagine that the method of WEBER¹) would be applicable to investigations at high pressures which this writer applied to the measurement of the velocity of diffusion of electrolytes in water (involving determinations of e.m.f.). A careful analysis of the difficulties involved in this method brought us to the conclusion not to apply it in this case. Also the systems that he investigated, electrolytes dissolved in water, are of so complicated a nature, and so many factors involved therein alter under pressure (one might mention e.g. the degree of dissociation, the hydration of the diffusing substance, and the polymerisation of the water), that it does not appear at all probable that we shall be in a position, in the near future, to draw any definite conclusions from the pressure-effect observed.

3. The solutions of many metals in mercury are of a much simpler type. The solvent is considered in general to be non-associated, whilst the dissolved metals are present in the monatomic condition.

4. We have applied, for such measurements at high pressures, the potentiometric method for the determination of the velocity of diffusion of metals in mercury described in our previous communication, choosing again cadmium for the diffusing metal.

We carried out the determinations (at 20°.00 C.) at 1 atm. and 1500 atm. pressure. Since preliminary investigations had shown that the change in D produced by a pressure of 1500 atm. was relatively small, it appeared to be superfluous to carry out measurements at intermediate pressures.

Actually the apparent deviations from a linear relationship between p and D are probably too small, considering the degree of accuracy of the measurements, to be determined with any certainty.

5. The determinations at 1500 atm. were carried out in precisely the same manner as at 1 atm. (see our previous paper), but with

¹⁾ Wied. Ann. N.F. 7, 469 (1879); Ook SEITZ, Wied. Ann. N.F. 64, 759 (1898).

this difference, that the diffusiometer in the steel cylinder (the pressure-bomb) (Fig. 3) was subjected to pressure by the introduction of oil.



Fig. 1.

We placed in the bomb a mixture of mineral oil with so much vaselin that the whole was fairly viscous at 20°. In this manner the pressure was maintained very constant during the experiment. The use of an automatic pressure device, similar to that which we are accustomed to utilize in our high-pressure investigations¹), is not allowable in diffusion experiments, since any kind of vibration must be avoided.

Through the use of the viscous oil-mixture we were able to

¹⁾ ERNST COHEN and R. B. DE BOER, Zeitschr. f. physik. Chemie 84, 41 (1913).

maintain the pressure so constant for several hours that it was only necessary now and then to regulate it by hand. This was always carried out about an hour before the measurements, whilst the diffusiometer was always brought up to 1500 atm. 12 hours before the beginning of the diffusion, so that, having regard to the high heat of compression, the apparatus should have ample opportunity to assume the temperature (20°.00 C.) of the thermostat. (With regard to temperature-regulation see the previous paper, § 10).

The pressure was read during the experiment on a manometer which was frequently checked by a pressure-gauge ¹).

6. With regard to the electrical measuring instruments reference should be made to the previous paper.

7. The diffusion-constant was calculated from the experimental data by means of the equation:

$$V\overline{D} = \frac{2 Ih}{cq V\overline{\pi}} (V\overline{t} - V\overline{t} - \theta).$$

Here the different symbols have the same significance as before (see the former paper, § 14).

8. We used the same diffusiometer at 1 atm. pressure as at 1500 atm. The value of $q = 8.419 \text{ cm}^3$ at 1 atm. (see § 15 of previous paper) must be corrected at 1500 atm. for the compressibility of the glass (2.2×10^{-6}) . We obtain $q_{1500 \text{ atm.}} = 8.400 \text{ cm}^3$.

9. It should be further remarked that in the calculation of the cadmium concentration c in mgm. per cc. of the amalgam (see § 16 of our previous communication) account must be taken of the compressibility of the extremely dilute amalgam at the high pressure, which we put equal to that of pure mercury (4×10^{-6}) . We obtain $d_{1500 \text{ atm.}}^{20.00^{\circ}} = 13.626$.

10. While for the determination of c at 1 atm. pressure we refer to our previous work, we remark that this quantity was also found at 1500 atm. by the measurement of the e.m.f. between the mercury surface and the standard electrode Am (Fig. 1 in the previous paper). We determined the relation between c and the e.m.f.

$$(E)_{1500 \text{ atm.}} = (E_{\bullet})_{1500 \text{ atm.}} - \left(\frac{RT}{nF} \log_e \sigma\right)_{1500 \text{ atm.}}$$

¹) ERNST COHEN, KATSUJI INOUYE and EUWEN, Zeitschr. f. physik. Chemie 75 257 (1910).

in precisely the same way as in the experiments at 1 atm. pressure. As a precautionary measure, the e.m.f. at 1 atm. was determined before every experiment that was carried out at 1500 atm., and after the pressure experiment the e.m.f. at 1 atm. was again determined after temperature equilibrium had been re-established in the diffusiometer.¹)

At each pressure the e.m.f. was tested for constancy during a period of several hours. At each measurement the pressure was read.

Table I contains the experimental results for 1 and for 1500 atmospheres respectively.³)

<i>Hg</i> in grammes	Time of electrol- ysis in min.	I in mA.	Cd deposited in mgm.	Conc. of amalgam mgm. per cc.	E _{latm.} in Volts	$\left(E_{0} ight) _{ m latm.}$ in Volts	E _{1500 atm.} in Volts	(E ₀) _{1500atm} in Volts
114.79	180	10.066	63.3 18	7.469	0 .05 778 5	0.08316 ¹	0.05562	0.081071
114.54	140	10.056	49 .19 ⁷	5.816	0.06093 ⁵	0.08315 ³	0.05877 ⁵	0.081068
114.53	1 0 5	10.041	36.844	4.356	0.064595	0.683166	0.06244	0.081086
111.21	100	10.029	35.045	4.267	0.06486	0.08317	0.06269	0.08107º
111.87	210	10.029	73.59 7	8.908	0.055555⁵	0.083154	0.05338	0.081054
						Mean: 0.08316		Mean: 0.08107

TABLE 1.²)

Temperature 20°.00 C.

Our equations for the calculation of c from the observed e.m.f. are therefore:

$$E_{1 atm.} = 0.08816 - \left(\frac{RT}{nF} \log_e c\right)_{1 atm.}$$
 or $E_{1 atm.} = 0.08316 - 0.029058 \log c_{1 atm.}$

and

$$E_{1500 atm.} = 0.08107 - \left(\frac{RT}{nF} \log_e c\right)_{1500 atm.}$$

or $E_{1500 atm.} = 0.08107 - 0.029058 \log c_{1500 atm.}$

11. Before we communicate our results for the final measurements at 1500 atm., we must make reference to the choice of the strength of current used in the electrolysis.

¹) Equilibrium in the amalgam of the standard electrode was also only established after a certain time had elapsed.

³) The values of $E_{1 atm.}$ and $(E_0)_{1 atm.}$ will also be found in Table I of our former communication.

It has already been noted that the value of the calculated coefficient of diffusion was not independent of the time during which the process of diffusion was followed after the completion of the electrolysis; also that there exists at 1 atm. pressure a range of values for the current-strength for a given concentration of the cadmium sulphate solution (we used one such that at 1 atm., as well as at 1500 atm., it contained 32 gm. $CdSO_4 . {}^{s}/{}_{s} H_{s}O$ per 100 gm. $H_{s}O$) within which the diffusion-constant is found independent of the time.

Meanwhile at 1500 atm. a greater current-strength must be chosen in order to reach this condition than e.g. at 1 atm. pressure. The explanation of this phenomenon is given by the fact that at a high pressure the meniscus of the mercury in the diffusiometer is more sharply curved. Our mode of treatment of the problem in the former paper (§ 21) thus receives fresh support. For the surface-tension of a mercury-water surface increases at a high pressure, as LYNDE¹) had shown.

It can be assumed that this is also the case for the system mercury-cadmium sulphate solution. Accordingly, with increase of pressure the size of the mercury surface will increase.

With a current-strength which will give a constant diffusioncoefficient at 1 atm. pressure, there will be found too high a value

t — 6.	E (Volt).	log c.	$D \times 10^5 \frac{\mathrm{cm}^2}{\mathrm{sec.}}$		
600	0.05478	0.90482	1.437		
1200	0 .05 595	0.86447	1.4 34		
1800	0.05 684	0.83391	1.435		
5400	0.06013 ⁵	0.72044	1.436		
6 60 0	0. 0 60 91	0.69387	1.440		
7200	0.06124	0.68251	1.437		
7800	0.061555	0.67158	1.436		
10800	0.06295	0.62366	1.436		
18000	0.06536	0.54064	1.435		
18900	0 .06559 ⁵	0.53255	1.433		
2880 0	0.06781	0.4564 0	1.436		

TABLE 2. $I = 4.785^6 \text{ mA}.$

¹) Phys. Rev. 22, 181 (1906).

for the coefficient at 1500 atm. pressure, when it is determined after the end of the electrolysis, since the concentration of the cadmium at the mercury surface will then be less than e.g. in the experiment at 1 atm. pressure.

The diffusion-coefficients which are calculated from the potential measurements carried out at later points of time will therefore always decrease until a limiting value is reached (vide § 21 of our previous paper). If we are concerned in obtaining at 1500 atm. also such conditions for the diffusion that the deviations may be

t — 6.	E (Volt).	log c.	$D \times 10^5 \frac{\mathrm{cm}^2}{\mathrm{sec.}}$
600	0.054765	0. 905 67	1.442
1200	0.05595	0.86439	1.445
1800	0.05685	0.83349	1.447
5400	0.06016	0.71950	1.452
6600	0.060917	0.69352	1.452
7200	0.06126	0.68173	1.452
7800	0.06158	0.67072	1.451
1 08 00	0.06297	0.62289	1.451
18000	0.06539	0.53961	1.451
18900	0.06563	0.53127	1.451
28800	0.06783	0. 45564	1.451
	÷.		

TABLE 3. $I = 4.751^8$ mA.

TABLE 4.

 $I = 4.737^7$ mA.

t — 0.	E (Volt).	log c.	$D \times 10^{5} \frac{\mathrm{cm}^{2}}{\mathrm{sec.}}$
600	0.05472	0.90671	1.426
1200	0.05591	0.86584	1.427
1800	0.056787	0.83564	1.425
18000	0.06534 ⁵	0.54115	1.432
18900	0.06559	0.53272	1.433
2880 0	0.06781	0.45 640	1. 431
	1		

exactly compensated, the current-strength must be taken at a higher figure. Tables 2-7 contain the experimental results for the measurements at 1500 atm.

In the experiment referred to in Table 4 some disturbance

1 - 7.020° IIIA.					
<i>t</i> — θ.	<i>E</i> (Volt).	log c.	$D \times 10^5 \frac{\mathrm{cm}^2}{\mathrm{sec.}}$		
600	0.05511	0.89337	1.448		
1200	0.056285	0.85294	1.445		
1800	0.05719	0.82188	1.449		
5400	0.06050	0.7078 8	1.454		
6600	0.061255	0 .68190	1.454		
7200	0.061605	0. 66985	1.456		
7800	0.061927	0.65875	1.455		
10800	0.06331	0.61118	1.453		
1800 0	0.065735	0.52773	1.455		
1890 0	0.06598	0.51930	1.455		
2 8 800	0.06818	0.4 4 359	1.456		
	1 1	1			

TABLE 5. $I = 4.628^9 \text{ mA}.$

TABLE	6.
I = 4.484	mA.

ι — θ.	<i>E</i> (Volt).	log c.	$D \times 10^{5} \frac{\mathrm{cm}^{2}}{\mathrm{sec.}}$			
600	0.05556	0.87781	1.459			
1200	0 .05673⁵	0.83745	1.457			
1800	0. 0 5762	0.80709	1.456			
5400	0.060917	0.69352	1.458			
6600	0.06167	0.66762	1.457			
7200	0.06201	0.65592	1.456			
7800	0.06234	0.64448	1.458			
10800	0. 06373	0.59673	1.459			
18000	0.06614	0.51371	1.456			
18 900	0.066385	0.505 37	1.456			
28800	0.06858	0.42991	1.455			
	1					

occurred at the start, which became noticeable in the measurement of the e.m.f. Since this vanished later, we nevertheless give the results of the experiment here. As will be evident, this experiment will have only a small effect on the combined result.

t — 0.	E (Volt).	log c.	$D \times 10^{5} \frac{\mathrm{cm}^{2}}{\mathrm{sec.}}$		
600	0.05565	0.87472	1.448		
1200	0.05682	0. 834 6 0	1.444		
1800	0.05769	0.80458	1.441		
5400	0.06099	0.69102	1.443		
6600	0.06175	0.66488	1.444		
7200	0.06209	0.65318	1.443		
7800	0.0624 2	0.64190	1.444		
10800	0.06380	0.59432	1.442		
18000	0.06621	0.51139	1.440		
18900	0.066455	0.50 296	1.441		
28800	0.0 68 65	0.42750	1.439		
	l				

TABLE 7. $I = 4.435^7 \text{ mA}.$

12. In Table 8 the results of experiments at 1 atm. (vide our previous paper, Table 16) and at 1500 atm. are collected.

TABLE 8.Temperature 20°.00 C.

Pressur	e 1 Atm.	Pressure 1500 Atm.		
Current strength in mA. $D \times 10^{5} \frac{\mathrm{cm}^{2}}{\mathrm{sec.}}$		Current strength in mA.	$D \times 10^{s} \frac{\mathrm{cm}^{2}}{\mathrm{sec.}}$	
3.6735	1.52 3	4.7856	1.436	
3.6178	1.518	4.7518	1.451	
3.6004	1.509	4.7377	1.432	
3.574	1.515	4.6289	1.455	
3.3957	1.515	4.4840	1.457	
3.018 ⁸	1.530	4.4357	1.442	
Mean $D_{1 ext{ atm.}}^{20^{\circ}.00} = 1.52$	of all: $20 \times 10^{-5} \frac{\text{cm}^2}{\text{sec.}}$	Mean $D_{1500 \text{ atm.}}^{20^{\circ}.00} = 1.4$	of all: 46 $\times 10^{-5} \frac{\text{cm}^2}{\text{sec.}}$	

We find therefore that the coefficient of diffusion of cadmium in mercury at $20^{\circ}.00$ C. decreases with increase of pressure, actually by 5 per cent, for an increase of pressure of 1500 atm.

SUMMARY.

The velocity of diffusion of cadmium in mercury at 20°.00 C. and at a pressure of 1500 atm. has been determined according to the method described in the preceding communication.

By an increase of pressure of 1500 atm. this velocity of diffusion is depressed by about 5 per cent.

Utrecht, March 1924.

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