to be the case, that the high temperature rate, A_1, in the neighborhood of the transition point, would differ from the low temperature rate, A_2, by a factor somewhat greater than 2. For if all the oxygen in the carbon dioxide that reacts goes to the monoxide, the high temperature rate must be represented by

$$C + CO_2 \longrightarrow 2CO$$

from which the factor 2 arises. In addition, since the carbon surface is cleaned up by the increased rate of decomposition, an increased rate of reaction is to be expected due to the increased availability of active surface. The latter consideration also accounts for the increased temperature coefficient, since the average energy of the surface available for reaction would be increased by the loss of the solid oxide, which was, presumably, most stable on the least saturated portions of the surface. Thus the high temperature rate A_1 may perhaps be represented by

$$C + CO_2 \longrightarrow CO + C\text{—}O_{\text{solid}}$$
$$C\text{—}O_{\text{solid}} \longrightarrow CO$$

where the second reaction follows so rapidly on the first that there is no accumulation of the solid oxide.

Summary

1. The measurement of the rate of a rapid heterogeneous reaction which usually is governed by diffusion conditions has been considered from a theoretical viewpoint. This discussion led to the development of a method which was used to determine the rate of reduction of carbon dioxide by graphite. The method involves the elimination of concentration gradients by increasing the gas velocity across the reacting surface until the velocity coefficient of the observed rate of reaction vanishes.

2. The rate of reduction of carbon dioxide has been measured in terms of cubic centimeters of carbon monoxide at N. T. P. produced per second from carbon dioxide at one atmosphere in contact with one square centimeter of graphite surface. It is given, for temperatures between 950 and 1300°, by the equation

$$\log A_1 = 5.07 - (38{,}700/4.575\ T)$$

and for temperatures between 850 and 950°, by

$$\log A_2 = 3.40 - (32{,}360/4.575\ T)$$

3. The significance of the appearance of two stages in the oxidation of graphite by carbon dioxide and its relation to the surface oxide complex are discussed.

PITTSBURGH, PA. RECEIVED SEPTEMBER 11, 1933

[CONTRIBUTION FROM FERTILIZER INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

The Solubility of Hydrogen in Water at 0, 50, 75 and 100° from 25 to 1000 Atmospheres

BY R. WIEBE AND V. L. GADDY

This is a continuation of previous work.[1] The apparatus and method have been described. The hydrogen was 99.9 per cent. pure, the impurity being nitrogen. A correction was applied assuming that the amount of nitrogen dissolved was proportional to its mole fraction. Table I gives a summary of the experimental results; the previously published[1] values for the 25° isotherm are added for comparison. Figure 1 shows a plot of the results. A correction for the change of vapor pressure due to the gas pressure on the liquid was made in the manner already explained.[1] Table II shows values of the vapor pressure of water at 100° used in making this correction. These values are only approximate, but a relatively large error in the partial pressure of water will make only a small correction in the final results. The total experimental error amounts to a few tenths of a per cent.

By a sensitive method of plotting deviations, the experimental data were smoothed with respect to both pressure and temperature to obtain interpolated solubility values. The results obtained by such interpolation are given in Table III. It was thought that an extrapolation of the results at 25 atmospheres to lower pressures by means of Henry's law, when corrected for deviations from the perfect gas law, would yield fairly accurate values for the absorption coefficient at one atmosphere. The following table gives the extrapolated values in terms of the Bunsen and Ostwald absorption coefficients[2] and shows also

(1) Wiebe, Gaddy and Heins, *Ind. Eng. Chem.*, **24**, 823, 927 (1932). THIS JOURNAL, **55**, 947 (1933).

(2) For definitions see "I. C. T.," Vol. **III**, pp. 254–255.

TABLE I

ABSORPTION COEFFICIENTS (CC. OF GAS AT S. T. P. PER G. OF WATER) OF HYDROGEN IN WATER

Press. of hydrogen, atm.	No. of runs for low press. approach	Av. for low press. approach	No. of runs for high press. approach	Av. for high press. approach	Final values
		0.00 ± 0.03°			
25	7	0.5366	8	0.5360	0.5363
50	6	1.075	7	1.077	1.076
100	7	2.133	7	2.129	2.131
200	7	4.182	10	4.191	4.187
400	5	8.008	7	8.009	8.009
600	6	11.624	6	11.628	11.626
800	6	14.993	7	15.033	15.013
1000	6	17.973	7	18.029	18.001
		25.00 ± 0.1°			
25	6	0.436	11	0.436	0.436
50	11	.865	13	.868	.867
100	6	1.726	14	1.730	1.728
200	12	3.386	15	3.399	3.39
400	7	6.56	22	6.57	6.57
600	6	9.58	9	9.58	9.58
800	5	12.45	13	12.47	12.46
1000	11	15.16	25	15.23	15.20
		50.00 ± 0.05°			
25	7	0.4064	7	0.4069	0.4067
50	7	.808	6	.810	.809
100	6	1.611	5	1.612	1.612
200	6	3.165	6	3.165	3.165
400	7	6.161	6	6.170	6.166
600	6	9.006	6	9.028	9.017
800	6	11.741	6	11.729	11.735
1000	6	14.389	6	14.419	14.404
		75.00 ± 0.05°			
25	7	0.4135	6	0.4136	0.4136
50	6	.8255	6	.8256	.8256
100	6	1.643	6	1.643	1.643
200	6	3.239	5	3.241	3.240
400	6	6.303	5	6.313	6.308
600	7	9.213	6	9.227	9.220
800	6	11.994	5	12.011	12.003
1000	6	14.677	6	14.694	14.686
		100.00 ± 0.05°			
25	6	0.4601	6	0.4629	0.4615
50	7	.9099	7	.9132	.9116
100	6	1.804	7	1.806	1.805
200	6	3.544	5	3.544	3.544
400	6	6.840	7	6.841	6.841
600	6	9.984	7	10.003	9.994
800	6	12.967	7	12.993	12.980
1000	8	15.764	14	15.785	15.775

TABLE II

Gas pressure on water, atm.	Vapor pressure of water, atm.	Gas pressure on water, atm.	Vapor pressure of water, atm.
25	1.018	400	1.40
50	1.04	600	1.66
100	1.09	800	1.97
200	1.19	1000	2.35

for comparison the values of Winkler[3] and at 25° an average value obtained from a table of best results published by Drucker and Moles.[4] The value of Just was excluded from this average result since his values in general appear too high.[5] The agreement with Winkler is fair except at the higher temperatures where his accuracy was least. There is perfect agreement with the average value of Drucker and Moles. It should be pointed out that when extrapolating solubility data to high pressures, a correction for the imperfection of the gas applied to Henry's law may lead to greater error than if none had been applied. The agreement in the case of nitrogen, for instance, is improved, whereas the results for hydrogen will be made much worse.

Ipatiew and co-workers[6] have determined the

TABLE III

ABSORPTION COEFFICIENTS, CC. OF HYDROGEN (S. T. P.) PER G. OF WATER

Press. atm.	Temperature, °C.										
	0	10	20	30	40	50	60	70	80	90	100
25	0.5363	0.4870	0.4498	0.4263	0.4133	0.4067	0.4053	0.4093	0.4203	0.4385	0.4615
50	1.068	.9690	.8945	.8475	.8215	.8090	.8095	.8171	.8385	.8720	.9120
75	1.601	1.453	1.341	1.271	1.232	1.212	1.211	1.224	1.254	1.298	1.355
100	2.130	1.932	1.785	1.689	1.638	1.612	1.610	1.628	1.667	1.727	1.805
150	3.168	2.872	2.649	2.508	2.432	2.395	2.393	2.422	2.485	2.576	2.681
200	4.187	3.796	3.499	3.311	3.210	3.165	3.168	3.208	3.286	3.402	3.544
300	6.139	5.579	5.158	4.897	4.747	4.695	4.692	4.746	4.866	5.042	5.220
400	8.009	7.300	6.766	6.430	6.245	6.166	6.173	6.249	6.392	6.600	6.841
500	9.838	8.980	8.328	7.922	7.705	7.613	7.625	7.717	7.885	8.129	8.429
600	11.626	10.610	9.856	9.390	9.135	9.017	9.016	9.131	9.324	9.665	9.994
700	13.370	12.214	11.362	10.818	10.524	10.389	10.405	10.527	10.757	11.093	11.512
800	15.013	13.746	12.808	12.218	11.889	11.735	11.746	11.893	12.169	12.555	12.980
900	16.548	15.215	14.217	13.583	13.230	13.072	13.084	13.233	13.533	13.946	14.394
1000	18.001	16.623	15.592	14.928	14.569	14.404	14.407	14.557	14.867	15.303	15.775

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[3] Winkler, *Ber.*, **24**, 89 (1891); Landolt and Börnstein, "Tabellen," Vol. **1**, **1923**, pp. 763–764.

[4] Drucker and Moles, *Z. physik. Chem.*, **75**, 405 (**1911**).

[5] See J. Horiuti, *Sci. Papers Inst. phys. chem. Res.* (*Tokyo*), No. 341, p. 218.

[6] Ipatiew, Jr., Drushima-Artemowitch and Tichomirow, *Ber.*, **65**, 568 (1932).

solubility of hydrogen in water at various temperatures up to 45° and at 100 atmospheres besides a slightly more extended range at 25°. Their values are somewhat lower than the ones obtained in this work. They encountered difficulties at higher temperatures and deduced from their unpublished high temperature results the possibility of a minimum for the Bunsen absorption coefficient between 65 and 75°.

TABLE IV

Temp., °C.	Extrapolated values	Winkler	Drucker and Moles
Bunsen absorption coefficient (cc. H_2 at S. T. P. per cc. of water) = α			
0	0.02177	0.02148	
10	.01976	.01955	
20	.01822	.01819	
25	.01774	.01754	0.01773
30	.01722	.01699	
40	.01663	.01644	
50	.01630	.01608	
60	.01615	.01600	
70	.01622	.0160	
80	.01655	.0160	
90	.01714	.0160	
100	.01791	.0160	
Ostwald absorption coefficient = $\alpha T/273.16$			
0	0.02177	0.02148	
10	.02048	.02019	
20	.01955	.01952	
25	.01936	.01915	0.01935
30	.01911	.01886	
40	.01907	.01885	
50	.01928	.01902	
60	.01970	.01951	
70	.02038	.02010	
80	.02140	.02068	
90	.02279	.02127	
100	.02447	.02186	

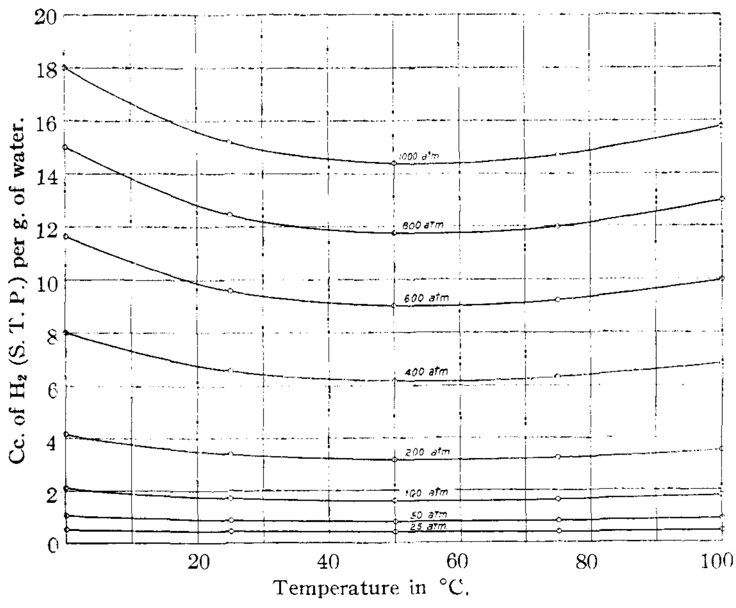

Fig. 1.

As Fig. 1 clearly shows the absorption coefficient (cc. of gas at S. T. P. per g. of water) shows a minimum. It should be pointed out, however, as has already been done by Just for instance,[7] and as shown in Table IV, that the minima obtained by differently defined absorption coefficients are not identical. In some cases one coefficient may in fact show a minimum while the other may not.

It might be desirable to comment briefly on the temperature coefficient of solubility. Hildebrand[8] states that on the basis of Raoult's law the solubility of a gas diminishes with rise in temperature. For gases above their critical temperatures this rule is very unreliable even qualitatively. In the nearly "ideal" case of hydrogen in benzene, the solubility of hydrogen increases with rise in temperature. For hydrogen in water, *e. g.*, the solubility diminishes only over part of the range.

Tammann[9] attempted to explain the existence of minima in water on the basis of a hydration theory. But since minima occur in solvents other than water[10] such special assumptions would not seem necessary.

Since Ostwald's absorption coefficient in dilute solutions should approach one practically at the critical temperature of the solvent[11] it would seem that all gases whose solubility diminishes with temperature over the known range should show a minimum at some higher temperature, while those whose solubility is known to increase with temperature might be thought to have passed the point of minimum at some lower temperature. Horiuti,[12] taking his own extensive data on the solubilities of hydrogen, nitrogen, carbon monoxide, oxygen and methane in various organic solvents, plotted the logarithm of the

(7) Just, *Z. physik. Chem.*, **37**, 342 (1901).

(8) Hildebrand, "Solubility," The Chemical Catalog Co., Inc., New York, 1924, p. 35.

(9) G. Tammann, *Z. anorg. allgem. Chem.*, **158**, 17 (1926); *ibid.*, **194**, 159 (1930).

(10) See, *e. g.*, oxygen in ethyl ether and methane in chlorobenzene in J. Horiuti, Ref. 5, pp. 215, 217.

(11) See, *e. g.*, G. Jäger, *Sitzungsber. Akad. Wiss. Wien*, Abt. 11A, **124**, 287 (1915).

(12) J. Horiuti, Ref. 5, pp. 206–217.

Ostwald coefficient against the reciprocal of the absolute temperature and extrapolated to the critical temperature of the solvent. Several of his curves show a minimum within the experimental range and others may be expected to do so on the basis of their curvature. It seems, therefore, as was pointed out by Kuenen,[13] that solubility minima are a phenomenon that can be deduced from the known behavior of mixtures and that the occurrence of minima is not necessarily dependent on the specific properties of the solvent or solute.

Finally a few words on attempts to calculate the solubility of gases, theoretically, may also be of interest. Van der Waals,[14] using his conception of a simple substance whose equation of state is identical with that of the particular mixture to be treated, attempted to calculate the solubility of nitrogen in water using his equation of state. He obtained a value much too small and attributed this to the association of water and not to the various assumptions needed for the computation. Later on he[15] pointed out that a correction for association would improve the agreement. Horiuti[16] using empirical relations applied van der Waals' idea to the solubilities of gases in organic liquids. For gases above their critical temperatures, he was able to get only the right order of magnitude.

Summary

The solubility of hydrogen in water at 0, 50, 75 and 100° and from 25 to 1000 atmospheres has been determined. The solubility of hydrogen in water shows a minimum within the experimental range similar to that of nitrogen in water.

Existing data seem to show that minima are a general phenomenon that can be deduced from the known behavior of mixtures and not necessarily dependent on specific properties of the solvent or solute.

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[13] Kuenen, *Proc. Roy. Soc. Edinburgh*, **23**, 312 (1900); Kuenen, "Verdampfung und Verflüssigung von Gemischen," Verlag Johann Ambrosius Barth, Leipzig, 1906, p. 82.

[14] Van der Waals–Kohnstamm, "Lehrbuch der Thermodynamik," Verlag Johann Ambrosius Barth, Leipzig, 1912, Vol. II, pp. 132–172.

[15] Van der Waals–Kohnstamm, Ref. 14, pp. 627–629.

[16] J. Horiuti, Ref. 5, pp. 225–252.

WASHINGTON, D. C. RECEIVED SEPTEMBER 11, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Heats of Solution and Heats of Reaction in Liquid Ammonia. I

BY CHARLES A. KRAUS AND JOHN A. RIDDERHOF[1]

I. Introduction

Data relating to heats of solution of electrolytes in solvents other than water are almost completely lacking. There are available only several observations of Pickering[2] on the heat of solution of sodium iodide and lithium nitrate in alcohol. Both salts have markedly higher heats of solution in alcohol than in water. It seemed desirable to have data as to the heat of solution of salts in solvents other than water, particularly in solvents of lower dielectric constant. Ammonia seemed a very suitable solvent for this purpose, since many common salts are readily soluble in ammonia, while a good many important substances are soluble in ammonia that are not soluble in water. Numerous reactions, moreover, may be carried on in liquid ammonia which cannot be carried out in water; for example, reactions involving the alkali metals. In the present paper we report the results of a general survey of the field.

II. Apparatus and Method

Method.—Because of its high volatility, it is not possible to make calorimetric measurements with liquid ammonia according to the methods that may be employed in the case of water or other non-volatile liquids. It seemed possible, however, that by determining the ammonia vaporized as a result of the heat effect, the heat effect itself might be determined from the known heat of vaporization of liquid ammonia.

There are, of course, other effects entering, such as a change in the temperature of the calorimeter and its contents. These temperature changes are most conveniently measured by means of a suitable thermocouple. Since the boiling point of liquid ammonia is −33.35°, it was obviously necessary to employ a vacuum-jacketed calorimeter. For this purpose a vacuum-jacketed tube was employed, surrounded by a bath of boiling ammonia. Since the amount of ammonia evaporated gives the principal datum in connection with a determination of the heat effect, it is necessary to establish equilibrium between the liquid and the vapor. For this purpose, a stirrer must be provided which agitates the liquid–vapor

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[1] Du Pont Fellow in Chemistry at Brown University.

[2] Pickering, *J. Chem. Soc.*, **63**, 865 (1888).