minations on about 0.2 g. of copper each, gave, respectively, errors of +0.0002 and −0.0004 g. The presence of nitric acid in small amounts also has no effect. Adding 1 cc. of concentrated nitric acid in each of two determinations, in an initial volume of 20 cc., one (using a volume buret) gave an error of +0.0003 g. and the other (weight buret) an error of +0.0002 g. This is of interest merely in showing that the complete elimination of nitric acid is unnecessary in the first evaporation with sulfuric acid, an operation which is sometimes troublesome on account of spattering.

Summary

A modification has been suggested, in the iodimetric determination of copper, which consists in adding a soluble thiocyanate near the end-point of the usual titration. Under these conditions, a further small liberation of free iodine occurs, and the reaction runs to a very sharp end-point. The precipitate at the end-point is white. The reaction takes place in stoichiometric proportions within about one part in sixteen hundred, so that the method appears to be comparable in accuracy with the best volumetric methods.

NEW HAVEN, CONN. RECEIVED FEBRUARY 26, 1935

[CONTRIBUTION FROM FERTILIZER INVESTIGATIONS UNIT, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

The Solubility of Helium in Water at 0, 25, 50 and 75° and at Pressures to 1000 Atmospheres[1]

BY R. WIEBE AND V. L. GADDY

The solubility of helium in water was measured for the purpose of obtaining a more general picture of the behavior of gases in water solution. The apparatus and method have been described previously.[2] The helium was 99.95% pure and was furnished by the Amarillo Helium Plant of the U. S. Bureau of Mines. It was found that a 1% nitrogen impurity had a very decided effect in raising the solubility but that the effect due to 0.05% was well within our experimental error. The results are given in Table I. Two or three series of runs were made at each temperature and pressure. Each series is represented by a line of figures in the table. The probable errors were estimated in the usual fashion from the equation

$$E = 0.674\sqrt{\Sigma\Delta^2/n(n-1)}$$

The partial pressures in column 1 were calculated as follows: Using the Poynting relation[3] the effect of the gas pressure on the vapor pressure of water was determined. These calculated vapor pressures were used to correct the measured total pressure for the presence of water vapor. Since the vapor pressures of water at 0, 25, 50 and 75° are 0.006, 0.031, 0.12 and 0.38 atm., respectively, the correction even at 75° and 1000 atm., where the worst deviation might be expected, would hardly be more than a few hundredths of 1%.

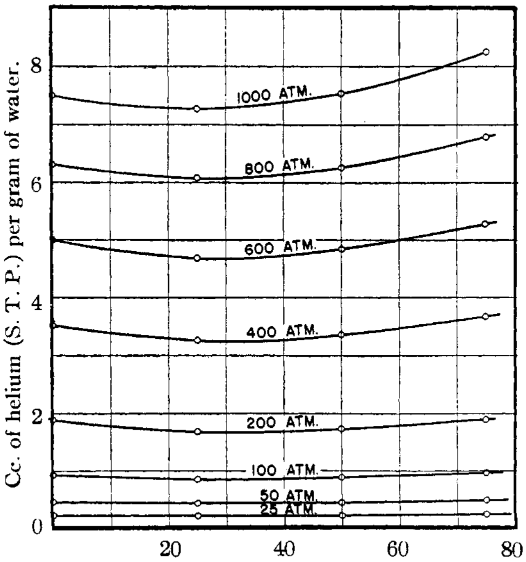

Fig. 1.

The main sources of error are in the sampling procedure and in measuring the exact equilibrium pressure. The solubility isobars in Fig. 1 show the same general trend with temperature as nitrogen and hydrogen.[2,4]

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[1] Read at the meeting of the American Chemical Society, New York City, April 23–27, 1935.

[2] Wiebe, Gaddy and Heins, THIS JOURNAL, **55**, 947 (1933).

[3] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, 1923, p. 183.

[4] Wiebe and Gaddy, THIS JOURNAL, **56**, 76 (1934); Saddington and Krase, *ibid.*, **56**, 353 (1934).

TABLE I

ABSORPTION COEFFICIENT OF HELIUM IN CC. OF GAS (S. T. P.) PER G. OF WATER

Partial press. helium, atm.	Absorption coefficient								Average
					0°				
25			0.2327	0.2316	0.2325	0.2321			
			.2309	.2332	.2313	.2336	0.2319		0.2322 ± 0.0002
50			.4652	.4674	.4647	.4669	.4701		
				.4654	.4670	.4692			
			.4677	.4679	.4676	.4697			.4674 ± .0003
100			.9281	.9213	.9231	.9250			
			.9225	.9267	.9253	.9200			.9240 ± .0008
200			1.805	1.806	1.811	1.805			
			1.811	1.801	1.819	1.803	1.801		1.807 ± .001
400				3.438	3.434	3.440			
				3.426	3.441	3.434			3.436 ± .002
600			4.911	4.910	4.925	4.926			
			4.914	4.911	4.903	4.924			4.916 ± .002
800			6.239	6.246	6.227	6.231			
			6.212	6.207	6.221	6.249	6.219		6.228 ± .003
1000			7.407	7.408	7.418	7.429	7.436		
	7.439	7.446	7.428	7.447	7.402	7.411	7.413	7.394	7.421 ± .003
					25°				
25			0.2189	0.2144	0.2142	0.2176			
			.2133	.2154	.2152	.2145	0.2147		
			.2163	.2195	.2227	.2091	.2127		0.2156 ± 0.0004
50				.4351	.4294	.4312			
			.4314	.4337	.4375	.4333	.4344		.4332 ± .0006
100			.8470	.8525	.8507	.8476			
			.8481	.8475	.8500	.8495			.8491 ± .0005
200			1.691	1.693	1.691	1.685	1.685		
			1.686	1.687	1.695	1.686	1.677		1.688 ± .003
400			3.236	3.243	3.228	3.250	3.241		
			3.237	3.246	3.249	3.239	3.239		3.241 ± .005
600			4.686	4.685	4.679	4.679			
			4.677	4.675	4.688	4.690	4.682		
			4.672	4.673	4.682	4.691			4.681 ± .004
800			6.020	6.015	6.006	6.012			
			6.035	5.996	6.011	6.015	6.022		6.015 ± .002
1000			7.251	7.258	7.284	7.262	7.271		
			7.254	7.290	7.255	7.273	7.230		7.263 ± .004
					50°				
50		0.4485	0.4467	0.4408	0.4401	0.4425	0.4445		
		.4451	.4472	.4456	.4435	.4449	.4443		0.4445 ± 0.0005
100				.8804	.8852	.8860			
		.8816	.8792	.8788	.8860	.8830	.8843		.8827 ± .0006
200		1.734	1.738	1.739	1.736	1.742	1.740	1.738	
			1.730	1.724	1.733	1.724	1.726		1.734 ± .004
400			3.382	3.346	3.345	3.356			
			3.353	3.371	3.340	3.370			3.358 ± .004
600			4.850	4.839	4.848	4.833			
			4.829	4.847	4.829	4.851	4.854		4.844 ± .002
800			6.276	6.190	6.253	6.281	6.269		
			6.228	6.250	6.247	6.237			6.248 ± .006
1000			7.541	7.528	7.508	7.548			
				7.548	7.541				7.536 ± .004
					75°				
25			0.2448	0.2459	0.2444	0.2441			
			.2431	.2448	.2429	.2449	0.2428		0.2442 ± 0.0002

TABLE I (*Concluded*)

Partial press. helium, atm.	Absorption coefficient 75°					Average
50	0.4920	0.4895	0.4897	0.4881	0.4861	
	.4856	.4897	.4894	.4923		0.4892 ± 0.0005
100		.9698	.9698	.9695		
	.9671	.9706	.9662	.9742	.9720	.9699 ± .0006
200	1.905	1.903	1.906	1.915		
		1.906	1.909			1.907 ± .004
400	3.656	3.672	3.667	3.671	3.688	
	3.645	3.657	3.665	3.667	3.672	3.666 ± .002
800	6.778	6.764	6.798	6.784		
	6.764	6.809	6.794	6.806		6.787 ± .004
1000	8.235	8.242	8.275	8.263		
	8.228	8.278	8.217	8.270		8.251 ± .006

The minimum for helium in water falls at about 30° whereas for hydrogen and nitrogen it is at about 55 and 70°, respectively. It will be remembered that Kuenen[5] predicted that the relatively less soluble gases should show a minimum at a lower temperature. This is at least true for helium. The temperatures at which the minima occur are in the same order as the critical temperatures of the respective gases. The shift of the minimum with pressure apparently is slight.

The ratios of S/p, where S is the number of cc. of helium measured at S. T. P. dissolved in one gram of water and p the partial pressure of helium, are given in Table II. The substitution of the ratio S/f for S/p in Table II would show a much greater variation along isotherms from 25 to 1000 atm., since at 0° and 1000 atm., *e. g.*, the fugacity of helium is about 1620 atm.

TABLE II

Partial pressure of helium	S/p 0°	25°	50°	75°
25	0.00929	0.00863		0.00976
50	.00935	.00866	0.00888	.00978
100	.00924	.00849	.00883	.00970
200	.00904	.00842	.00867	.00954
400	.00859	.00810	.00839	.00917
600	.00819	.00780	.00807	
800	.00779	.00752	.00781	.00849
1000	.00742	.00726	.00754	.00825

It will be seen that the ratios show little variation below 50 atm. For this reason the averages of the 25 and 50 atm. values were used to compute the Bunsen and Ostwald absorption coefficients.[6] This procedure may seem somewhat arbitrary but the error involved cannot in any case be great.

Table III gives a comparison between Bunsen and Ostwald's absorption coefficients for the data of Cady and co-workers,[7] of Lannung[8] and of the present work. The agreement is very good considering the difficulties of measurements at low pressures. The 30° point of Cady and co-workers is admittedly uncertain. Their individual values vary greatly at this point and they mention the softening of stopcock grease as a possible source of error.

TABLE III

°C.	Wiebe and Gaddy	Cady, Elsey and Berger	Lannung
Bunsen Absorption Coefficient = α			
0	0.00932		
2		0.00937	
15		.00884	0.0089
25	.00860	.00861	.0087
30		.00836	.00856
50	.00877		
75	.00951		
Ostwald Absorption Coefficient = $\alpha(T/273.16)$			
0	0.00932		
2		0.00944	
15		.00933	0.0094
25	.00939	.00940	.0095
30		.00928	.0095
50	.01037		
75	.01212		

Figures 2 and 3 show plots of the Bunsen and Ostwald absorption coefficients *vs.* temperature, respectively. The smooth curves were drawn through our own data. The plot shows that the minimum for the Bunsen absorption coefficient is just beyond the range of the previous investigators but that the one for the Ostwald coefficient if it exists at all apparently lies at or below 10°. The present instance shows again as was pointed out by Just[9] that the minima obtained by differently defined absorption coefficients are not identical.

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[5] Kuenen, "Verdampfung und Verflüssigung von Gemischen," Verlag Johann Ambrosius Barth, Leipzig, 1906, p. 82.

[6] For definition see "I. C. T.," Vol. III, pp. 254–255.

[7] Cady, Elsey and Berger, THIS JOURNAL, **44**, 1456 (1922).

[8] Lannung, *ibid.*, **52**, 68 (1930).

[9] Just, *Z. physik. Chem.*, **37**, 342 (1901).

The data of Antropoff[10] and Estreicher[11] have not been included since they are greatly in error. Their sources of error were thoroughly discussed by Cady and co-workers.[7] Valentiner[12] after correcting his previous errors attempted to apply the Clausius–Clapeyron equation, assuming ideal conditions, to insufficient data. Since he placed too much emphasis on the 30° point of Cady, his equation is without significance.

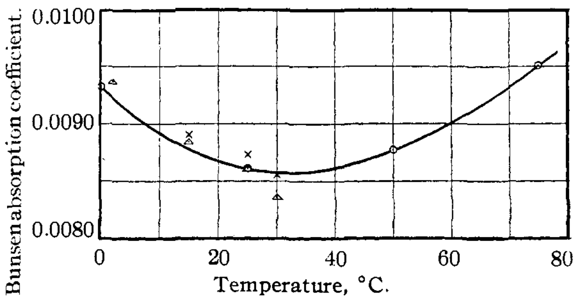

Fig. 2.—⊙, Wiebe and Gaddy; △, Cady, Elsey and Berger; ×, Lannung.

If the Ostwald absorption coefficient is calculated from the present data at 0°, corrected for the compressibility of water and helium, the following table is obtained.

TABLE IV

OSTWALD ABSORPTION COEFFICIENT AT 0°

Partial pressure of helium	25	50	100
$\frac{\text{Concn. of He in water}}{\text{Concn. of He in gas phase}}$	0.00941	0.00961	0.00977
Partial pressure of helium	200	400	600
$\frac{\text{Concn. of He in water}}{\text{Concn. of He in gas phase}}$	0.01007	0.01048	0.01095
Partial pressure of helium	800	1000	
$\frac{\text{Concn. of He in water}}{\text{Concn. of He in gas phase}}$	0.01124	0.01151	

The results of Table IV show that the corrected Ostwald absorption coefficient for helium is far from remaining constant. In a previous publication[2] the solubilities of nitrogen in water at 25 and 50° were calculated by assuming the one atm. value of the coefficient to remain constant throughout the pressure range. It was found that the calculated solubility isotherms intersected the experimental ones at some pressure, giving a fair agreement over some parts and in other parts deviations of as much as 25%. These examples show that the corrected Ostwald coefficient could not be used with any degree of reliability to calculate the high pressure solubilities of a gas from experimental values obtained at low pressures.

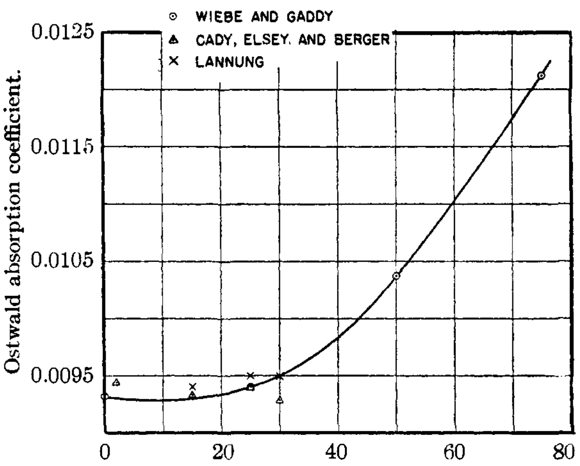

Fig. 3.

Table V gives a summary of both the experimental and interpolated values. The latter values were obtained by plotting deviations from an equation of the type

$$S = ap + bp^2 + cp^3$$

where S is the solubility, a, b, c are constants and p the partial pressure of helium. Since the deviations were small, the interpolated results should be dependable.

TABLE V

SUMMARY OF RESULTS

* Interpolated values

Partial pressure of helium in atm.	Solubility in cc. at S. T. P. per g. of water 0°	25°	50°	75°
25	0.2322	0.2156	0.2225*	0.2442
50	.4674	.4332	.4445	.4892
75	.6973*	.641*	.6645*	.7308*
100	.9240	.8491	.8827	.9699
150	1.371*	1.270*	1.301*	1.443*
200	1.807	1.688	1.734	1.907
300	2.643*	2.479*	2.552*	2.805*
400	3.436	3.241	3.358	3.666
500	4.196*	3.975*	4.114*	4.489*
600	4.916	4.681	4.844	5.277*
700	5.591*	5.361*	5.559*	6.038*
800	6.228	6.015	6.248	6.787
900	6.838*	6.645*	6.907*	7.519*
1000	7.421	7.263	7.536	8.251

Hydrates of several of the inert gases of probable composition "Inert gas $5H_2O$" are known. Xenon forms a hydrate very readily, the dissociation pressure of the system hydrate, solution, and gas being in the neighborhood of one atmosphere

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(10) Antropoff, *Z. Elektrochem.*, **25**, 269 (1919).

(11) Estreicher, *Z. physik. Chem.*, **31**, 176 (1899).

(12) Valentiner, *Z. Physik*, **42**, 253 (1927); **61**, 563 (1930).

at 0°.[13] Krypton and argon also form hydrates, but not so readily as xenon; the dissociation pressures of their hydrates are, respectively, 14.5 and nearly 100 atm. at 0°.[14] While the hydrates of neon and helium have not yet been found, the present work indicates either that 1000 atm. at 0° is not enough pressure for the formation of helium hydrate or that the critical decomposition point is below 0°. The relative ease of hydrate formation of the inert gases is in line with their respective polarizabilities. Helium shows the lowest polarizability and should therefore be expected to have the highest dissociation pressure at any corresponding temperature.

We wish to express thanks to Messrs. C. W. Seibel and W. M. Deaton for the very pure helium used in this work.

Summary

The solubility of helium was measured at 0, 25, 50 and 75° from 25 to 1000 atmospheres partial pressures.

The calculated Bunsen and Ostwald absorption coefficients showed excellent agreement with the best known values.

Like hydrogen and nitrogen, helium also shows a minimum of solubility, though at a lower temperature.

WASHINGTON, D. C. RECEIVED FEBRUARY 27, 1935

[13] De Forcrand, *Compt. rend.*, **181**, 15 (1925).

[14] De Forcrand, *ibid.*, **176**, 355 (1923).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF RADCLIFFE COLLEGE]

A Revision of the Atomic Weight of Arsenic. The Ratio of Arsenic Trichloride to Iodine

BY GREGORY PAUL BAXTER AND LAURENCE DAVID FRIZZELL

In two recent investigations determinations of the ratios of arsenic trichloride and tribromide to silver[1] and of arsenic trichloride to iodine pentoxide have been described.[2] The atomic weight of arsenic derived from this work is 74.91. Below is described the determination of the ratio of arsenic trichloride to iodine.

The procedure in general followed that described for the determination of the ratio of arsenic trichloride to iodine pentoxide. Weighed amounts of arsenic trichloride after hydrolysis were allowed to react with nearly equivalent weighed amounts of iodine. The acid formed during the reactions was neutralized and the end-point found with very dilute standard solutions of arsenite and iodine.

Purification of Reagents

Water and hydrochloric acid were purified by distillation. Mono- and di-sodium phosphates, sodium and potassium iodides, di-sodium arsenate and potassium permanganate were subjected to several recrystallizations, with centrifugal drainage and rinsing of the crystals in a porcelain centrifuge. Pyrex vessels were employed and the solutions were initially clarified by filtration through sintered glass. The phosphates, large amounts of which were used in the analyses, were free from both reducing and oxidizing impurities such as iron.

The Preparation of Arsenic Trichloride

The method for preparing and purifying arsenic trichloride followed closely that described in the earlier papers.[1,2] The compound was synthesized from scrubbed and dried tank chlorine and commercial arsenic which had been freed from trioxide at a high temperature in a vacuum. After standing over arsenic crystals the trichloride was refluxed for some time in a column filled with arsenic crystals forming part of a previously exhausted glass system. It was then subjected to a series of twenty-three fractional distillations in previously exhausted systems. One or more light and heavy fractions were removed in each distillation. The apparatus employed resembled closely that used by Baxter and Shaefer and other investigators in similar work and is illustrated in Fig. 1. The bulb A containing the arsenic trichloride is connected with a Hempel column B filled with glass pearls and terminating in a special capillary valve C which could be opened at will by breaking the capillary with a magnetic hammer. Bulbs 3 and 39 served to collect light or heavy fractions after bending the capillaries through 180° and when filled were disconnected by sealing the capillaries. A receiving system of similar construction was attached through the capillary F and after exhaustion with a diffusion pump was connected to the still by breaking the special valve C. The earlier light and heavy fractions were rejected. Fractions analyzed are numbered in the order of decreasing volatility. Up to Fractions 14 and 15 the fractions collected were sealed off in bulbs as indicated in Fig. 1. Since the method of analysis precluded determination of the weight of the glass after the bulb was opened, the earlier fractions analyzed were transferred to bulbs the weights of which were known in advance by means of the system shown at E, Fig. 1. The bulb con-

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[1] Baxter, Shaefer, Dorcas and Scripture, THIS JOURNAL, **55**, 1054 (1933).

[2] Baxter and Shaefer, *ibid.*, **55**, 1957 (1933).