[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE ROYAL VETERINARY AND AGRICULTURAL COLLEGE]

THE SOLUBILITIES OF HELIUM, NEON AND ARGON IN WATER AND SOME ORGANIC SOLVENTS

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The distribution of a solute between two solvent media has been discussed recently in two papers by Bjerrum,[1,2] in which, especially, the relationship between the partition of electrolytes and non-electrolytes is treated according to the theoretical considerations of Born.[3] While the partition coefficient V of a non-electrolyte is defined as the ratio of its equilibrium concentrations in the two media, for a binary strong electrolyte, for example, sodium chloride

$$V_{\mathrm{NaCl}} = \sqrt{\frac{[\mathrm{Na}^+]^{\mathrm{II}}[\mathrm{Cl}^-]^{\mathrm{II}}}{[\mathrm{Na}^+]^{\mathrm{I}}[\mathrm{Cl}^-]^{\mathrm{I}}}}$$

where $[\mathrm{Na}^+]^{\mathrm{I}}$ denotes the concentration at equilibrium of the sodium ion in the medium I and so on.

The partition coefficient V_{n} of a non-electrolyte is related to A_{n} the reversible work of transferring one molecule from its solution in one medium to a solution of the same concentration in the other medium by the formula

$$A_{\mathrm{n}} = kT \log_e V_{\mathrm{n}}$$

For the binary electrolyte sodium chloride the corresponding relation is

$$A_{\mathrm{NaCl}} = 2kT \log_e V_{\mathrm{NaCl}}$$

where A_{NaCl} is the reversible work of transference of an ion pair $\mathrm{Na}^+ + \mathrm{Cl}^-$ from the one medium to a solution of the same concentration in the other. The transference work A_{NaCl} can be split into two parts, an electrical work due to the charge on the ions and a specific work depending on the configuration of the ions. This may be expressed by the equation

$$A_{\mathrm{NaCl}} = A_{\mathrm{n(Na^+)}} + A_{\mathrm{n(Cl^-)}} - E^{\mathrm{I}}_{(\mathrm{NaCl})} + E^{\mathrm{II}}_{(\mathrm{NaCl})}$$

where $A_{\mathrm{n(Na^+)}}$ and $A_{\mathrm{n(Cl^-)}}$ represent the transference work for molecules similar to Na^+ and Cl^- in all respects except in not being electrically charged, while $E^{\mathrm{I}}_{(\mathrm{NaCl})}$ and $E^{\mathrm{II}}_{(\mathrm{NaCl})}$ represent the electrical work of discharging the ion pair $\mathrm{Na}^+ + \mathrm{Cl}^-$ in the media I and II, respectively. As many ions may be regarded as spherical, E^{I} and E^{II} can be calculated by means of Born's Formula

$$E_{\mathrm{NaCl}} = \frac{\epsilon^2}{2D}\left(\frac{1}{r_{\mathrm{Na^+}}} + \frac{1}{r_{\mathrm{Cl^-}}}\right)$$

$r_{\mathrm{Na^+}}$ and $r_{\mathrm{Cl^-}}$ are the radii of the ions, $- \mp \epsilon$ their charges and D is the dielectric constant of the medium. The other work terms, $A_{\mathrm{n(Na^+)}}$

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[1] N. Bjerrum and E. Larsson, *Z. physik. Chem.*, **127**, 358 (1927).

[2] N. Bjerrum, *Trans. Faraday Soc.*, **23**, 77 (1927).

[3] M. Born, *Z. Physik*, **1**, 45 (1920).

and $A_{n(Cl^-)}$, cannot be calculated, but it is reasonable to suppose that they will be equal to the corresponding transference work for molecules of the inert gas type of the same size as Na^+ and Cl^-. In order to test this hypothesis it is of importance to have data for the partition coefficients of the inert gases between various solvents. With this end in view I undertook the present measurements at the suggestion of Professor Bjerrum.

Apparatus

Owing to the considerable difference between the solubilities of helium, neon and argon, apparatus of three different sizes were used. The design was based on that of v. Antropoff,[4] with certain improvements to increase the accuracy. In particular the glass spiral, used by v. Antropoff to enable the absorption bulb to be shaken independently of the rest of the apparatus, was dispensed with and the apparatus shaken as a whole; this had the double advantage on the one hand of considerably decreasing the undesirable dead space and on the other of making the apparatus less fragile and thus easier to handle.

The apparatus is shown diagrammatically in Fig. 1. The absorption bulb A had a capacity of 88, 310 and 587 cm.[3] in Apparatus I, II and III, respectively; the rest of the apparatus was substantially the same in all three. Behind the manometer BC, which also served as a gas buret, was a scale. The buret tube B had an internal diameter 0.5 cm., a length of 35 cm. and capacity of about 7 cm.[3] The apparatus was fixed in a 4-mm. thick aluminum frame with bands of brass or where desired of transparent celluloid; the siphon beyond a was free from the frame.

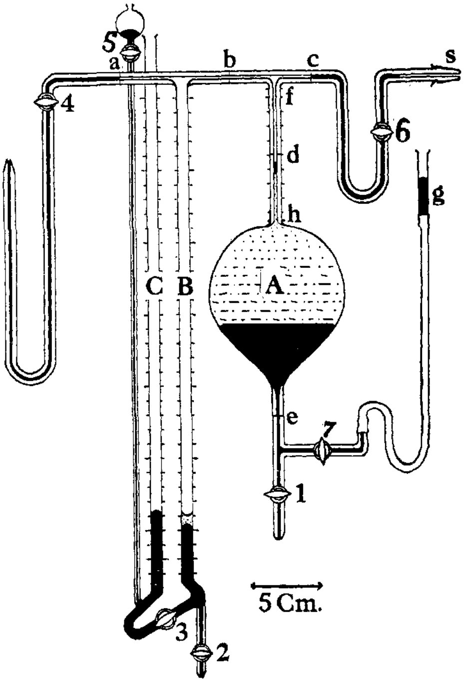

Fig. 1.

Calibration.—The apparatus was placed in a specially constructed air thermostat, whose temperature could be varied from 2 to 45° and kept constant to within ±0.03°. After evacuation through 6, mercury was let in through 1 until it filled the absorption bulb A and the capillary as far as b and c. By letting out mercury through 1 and weighing it the volume between b, c and d was determined; similarly the vertical capillary, which was graduated from f to h, was calibrated; finally, the volume of the absorption bulb from d to e was determined by the same method.

The coefficient of expansion of the glass was determined by measuring the capacity of the absorption bulb A at two different temperatures.

The gas buret was calibrated by a similar method from the marks a and b to the bottom by letting out mercury 0.2 cm.[3] at a time through 2.

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[4] v. Antropoff, *Z. Elektrochem.*, **25**, 269 (1919).

By reading through a telescope at a distance of 1 m. it was easy to attain an accuracy of 0.1 mm. or of 0.002 cm.^{3}

Technique.—Before each series of measurements the apparatus was cleaned throughout with a warm mixture of chromic and sulfuric acids. All the stopcocks except 6 were thoroughly smeared with Ramsay grease, the apparatus was evacuated through 6 and then, mercury being let in through 1, was filled completely as far as the open ends of the siphon tube, the manometer tube C and the movable reservoir g.

To the ground glass joint s was connected an L-tube the other end of which dipped into a bottle containing pure solvent, and solvent was drawn into A by letting mercury run out through 1. When A was half full of the solvent, the L-tube was disconnected from s, the stopcock 6 was quickly dried with cotton wool and greased. Half the remaining mercury was now let out through 1, while air dried over calcium chloride was sucked in through 6. The ground glass joint s was then connected through two drying towers containing sulfuric acid and bits of glass tubing to a manometer and an oil suction pump. By shaking the apparatus the mercury was set into wave-like motion; this facilitated the escape of air and vapor bubbles, which otherwise tended to collect at the mercury surface. When most of the air had been sucked away either bumping occurred or else vapor bubbles formed only at the surface; to reduce the loss of liquid by bumping, 6 was opened only at intervals. Usually the apparatus was kept evacuated overnight and after repeated shaking and suction through 6, one could show that all air had been removed by shaking for a time with 6 closed, letting mercury in through 7 so that the solvent surface was approximately at d and then opening 3, when the mercury would rush up the tube B, hitting the top with a metallic clang and then filling the rest of the tube as far as the solvent surface at d, no air bubbles being visible. If, on the other hand, an air bubble formed, the suction and test were repeated.

When the solvent was free from air and shut in as described in such a way that it nowhere was in contact with any stopcocks, the apparatus was placed in the air thermostat and brought to 20.0°, the temperature at which it was calibrated, the cock 3 being open. By opening 7 and moving the small reservoir g, the surface of the solvent could be kept in the vertical part of the capillary.

When the temperature was approximately correct, the apparatus was again taken out of the thermostat and the siphon tube sunk into a beaker filled with mercury; the gas which was stored over mercury in small glass vessels was sucked in through the siphon tube by closing 3 and opening 4 and 2. When the gas buret was nearly full, mercury was sucked from the beaker through the siphon tube to a, and 2 and 4 were then closed. Then by opening 7 and raising the reservoir g a few drops of solvent were pressed over into the gas buret in order to saturate the gas with the solvent vapor. After lowering the reservoir g until the solvent surface was at f and attaching rubber tubing to the glass joint s, a small quantity of mercury was blown over from the horizontal capillary to the surface of the solvent; the rest of the mercury was then sucked back to c, 3 was opened and by letting mercury out through 2 the mercury levels in the tubes B and C were adjusted to be approximately the same. The apparatus could now be brought to the exact temperature of the air thermostat without any fear of loss of gas through absorption. As the bulb A and vertical capillary hf constituted a very sensitive thermometer, it was easy to tell when temperature equilibrium was attained by the surface of the mercury in the capillary remaining steady. The height of the mercury and solvent surface in the buret tube as also that of the mercury in the open tube C were read through the telescope. The atmospheric pressure was read on a Fortinette Standard Barometer. From these data could be calculated *W*, the volume of the gas at standard temperature and pressure (S. T. P.).

Saturation of the solvent was brought about by letting out through 1 about 1 cm.^{3}

of mercury, which was weighed, and then putting the apparatus into the air thermostat, where it was mechanically shaken as a whole with the frame. The rate of shaking was adjusted to be in resonance with the natural period of swing of the liquid. As absorption took place the mercury rose in the buret tube B, but by opening 5 at intervals more mercury could be let into C so as to keep the levels in C and B approximately equal. When the liquid had reached saturation, which generally took about one hour, the liquid levels in B and C were again read; from these one can calculate directly the pressure of the gas remaining and also its volume, since the volume from d to the surface of the liquid in A is equal to the volume of the weighed mercury let out through 1 corrected by an amount equal to any change in the volume of the small quantity of the solvent in b.

The thermostat temperature was then altered and the measurements of pressure and volume were repeated after saturation was attained.

At the end of series of measurements the cock 3 was closed, the ground glass joint s was connected to the suction pump and the mercury in the capillary around 6 was sucked out. Air was let in through 6 and the mercury in A was let out through 1. The volumes of the solvent, the mercury and the bulb at the various temperatures were calculated from the volumes at 20° and the various coefficients of expansion. When necessary a small correction to the volumes of the liquids and bulbs was applied for the variation of pressure in the apparatus; this was generally avoided by measuring at pressures very near that of the atmosphere.

The Materials Employed.—The helium, neon and argon were bought from Linde's Liquid Air Factory. According to their specification the helium contained as impurity only 0.5% by volume of neon, the neon only 1% of helium and the argon only 0.5% of nitrogen. The densities of the argon and neon were in agreement with this; the spectrum of the helium showed faint neon lines. For the technique of handling and storing these gases the reader is referred to Travers, "The Experimental Study of Gases." A Töpler–Antropoff[4] pump was found to be especially convenient for this part of the work.

The water used had a specific conductivity 2×10^{-7}.

The methyl alcohol (Methanol B. A. S. F.) was distilled over magnesium strips freshly cut from a block.[5] The first third of the distillate was rejected.

The ethyl alcohol (Alcohol absolutus, Ph. dan.) was distilled twice over freshly prepared quick lime.[6]

The acetone (Kahlbaum's "zur Analyse") was used after showing the absence of water, aldehyde and acid.

The benzene was Kahlbaum's "zur Molekulargewichtsbestimmung" and had a melting point of 5.48°.

The cyclohexane, from Poulenc Frères, was shaken for a considerable time with fuming sulfuric acid, separated in a separation funnel and shaken with water until neutral. After keeping over phosphorus pentoxide for several days, it was distilled over phosphorus pentoxide; the first quarter was rejected and the remainder had a melting point of 6.0°. Cyclohexane of this purity was used for the solubility determinations of argon. Later the remainder was distilled over sodium and a fraction with a melting point of 6.3° was used; previously recorded melting points are 6.4[7] and 6.5°.[8]

Cyclohexanol "pur" from Poulenc Frères was fractionated twice *in vacuo;* the fractions used had melting points of 23.6 to 23.9°; E. Schreiner and O. E. Frivold[9] found a melting point of 23.9°.

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[5] N. Bjerrum and L. Zechmeister, *Ber.*, **56**, 894 (1923).

[6] Erik Larsson, "Inaugural Dissertation," Lund, **1924.**

[7] N. Zelinsky, *Ber.*, **34**, 2802 (1901).

[8] Sabatier and Senderens, *Compt. rend.*, **132**, 1255 (1901).

[9] E. Schreiner and O. E. Frivold, *Z. physik. Chem.*, **124**, 1 (1926).

Results

The absorption coefficient α as defined by Bunsen is given by the formula

$$\alpha = \frac{(W \div w)P_0}{W_L \times P}$$

where W is the volume at S. T. P. of the gas originally introduced; w is the volume at S. T. P. remaining after absorption; W_L is the volume of the

TABLE I

SOLUBILITY OF HELIUM

Solvent	Complete list of measurements of α 15.0°	20.0°	25.0°	30.0°	37.0°
Water	0.0089	0.0089		0.0086	
	.0088	.0087		.0086	
Methyl alcohol	.0297	.0312	0.0327	.0342	
	.0298	.0314			
Ethyl alcohol	.0270	.0281		.0304	
	.0266	.0283		.0309	
Acetone	.0279	.0295	.0319		
	.0285	.0310	.0332		
	.0284	.0309	.0331		
Benzene	.0165	.0180	.0193		
		.0180	.0192	.0201	
	.0165	.0179	.0190	.0200	
Cyclohexane	.0221	.0239		.0270	
	.0220	.0232		.0265	
Cyclohexanol			.0099	.0102	0.0117
			.0102	.0112	.0121

TABLE II

SOLUBILITY OF NEON

Solvent	Complete list of measurements of α 5.0°	10.0°	15.0°	20.0°	25.0°	30.0°	37.0°	45.0°
Water	0.0119	0.0115		0.0103	0.0102		0.0096	0.0094
	.0117	.0111		.0103			.0096	.0094
	.0119	.0113		.0105			.0098	
Methyl alcohol			0.0413	.0432			.0478	
				.0428		0.0460		
Ethyl alcohol			.0381	.0398			.0443	
			.0380	.0407	.0417			
Acetone			.0428	.0456	.0482			
				.0470	.0498			
			.0410	.0430	.0450			
Benzene		.0233		.0269			.0333	
		.0239		.0273			.0328	
Cyclohexane			.0334	.0354		.0393		
			.0327	.0353	.0373	.0391		
Cyclohexanol					.0151	.0160	.0169	
					.0153		.0174	

solvent at the temperature of saturation; P is the partial pressure of the gas in mm. of mercury and P_0 is 760 mm.

In Tables I, II and III are collected all of the results of the measurements in the Bunsen coefficient, α. For convenience of reference from these average values at 15, 18, 20, 25, 30 and 37° have been calculated, and collected in Tables IV, V and VI, the Ostwald partition coefficients, l, which

TABLE III

SOLUBILITY OF ARGON

Complete list of measurements[a] of α

Solvent				18.0°	20.0°	25.0°	35.0°	37.0°	40.0°
Water	$0.0505^{1.65}$		$0.0338^{19.9}$	0.0349		0.0315	0.0271	$0.0287^{30.0}$	0.0254
		$.0387^{12.4}$			0.0334				.0251
Methyl alcohol	$.259^{5.1}$	$.257^{8.0}$	$.254^{13.0}$		.249	.246		.240	
	$.259^{6.0}$	$.257^{8.0}$	$.254^{14.0}$	.251	.250	.245		.242	$.239^{45.0}$
		$.267^{8.0}$	$.254^{13.0}$	.250	.250	.245		.240	
Ethyl alcohol	$.248^{1.9}$			.242	.239	.237	.232		.235
					.238				
					.243				
EtOH–H_2O equivalent amounts		$.109^{12.5}$		.109			.110		
Acetone	$.268^{5.0}$		$.271^{14.0}$	.272		.274	.278		.281
		$.270^{10.0}$				.274	.278		
	$.269^{6.0}$		$.271^{13.0}$	.272	.272	.274		.279	
Benzene			$.220^{13.0}$	.220	.221	.222	.224		
			$.217^{14.0}$	.217	.217	.217	.219		
			$.219^{13.0}$	.221	.222	.223	.227		
Cyclohexane			$.308^{10.0}$	.307	.306	.305		.302	
			$.309^{10.0}$	.307	.307	.305		.305	
				.306	.306	.304		.301	
Cyclohexanol						.113		.115	$.117^{45.0}$
						.112		.114	$.116^{45.0}$
						.112		.113	$.114^{45.0}$

[a] Small superior figures on measurements indicate the temperatures at which they were made.

TABLE IV

SOLUBILITY OF HELIUM

Solvent		15°	18°	20°	25°	30°	37°
Water	α	0.0089	0.00885	0.0088	0.0087	0.0086	0.0084
	l	.0094	.0094	.0095	.0095	.0095	.0095
Methyl alcohol	α	.0298	.0307	.0313	.0328	.0343	.0364
	l	.0314	.0327	.0336	.0358	.0381	.0413
Ethyl alcohol	α	.0268	.0275	.0281	.0294	.0306	.0325
	l	.0283	.0293	.0302	.0321	.0340	.0369
Acetone	α	.0284	.0299	.0309	.0331	...	...
	l	.0300	.0319	.0332	.0361	...	...

TABLE IV (*Concluded*)

Solvent		15°	18°	20°	25°	30°	37°
Benzene	α	.0165	.0174	.0180	.0192	.0202	.0221
	l	.0174	.0186	.0193	.0210	.0224	.0251
Cyclohexane	α	.0220	.0227	.0236	.0252	.0268	.0293
	l	.0232	.0242	.0253	.0275	.0297	.0333
Cyclohexanol	α	...	...	...	.0100	.0107	.0119
	l	...	...	...	.0109	.0119	.0135

TABLE V

SOLUBILITY OF NEON

Solvent		15°	18°	20°	25°	30°	37°
Water	α	0.0108	0.0105	0.0104	0.0101	0.0099	0.0096
	l	.0114	.0112	.0112	.0110	.0110	.0111
Methyl alcohol	α	.0413	.0423	.0430	.0444	.0459	.0480
	l	.0436	.0451	.0462	.0485	.0509	.0545
Ethyl alcohol	α	.0381	.0394	.0402	.0417	.0433	.0442
	l	.0402	.0420	.0431	.0455	.0481	.0502
Acetone	α	.043	.045	.046	.048	...	...
	l	.045	.048	.049	.052	...	...
Benzene	α	.0254	.0264	.0271	.0288	.0306	.0330
	l	.0268	.0281	.0291	.0314	.0340	.0375
Cyclohexane	α	.0333	.0345	.0353	.0373	.0392	.0419
	l	.0351	.0368	.0379	.0407	.0435	.0476
Cyclohexanol	α	...	...	...	.0152	.0161	.0173
	l	...	...	...	.0166	.0179	.0196

TABLE VI

SOLUBILITY OF ARGON

Solvent		15°	18°	20°	25°	30°	37°
Water	α	0.0371	0.0349	0.0336	0.0314	0.0289	0.0264
	l	.0391	.0372	.0361	.0343	.0321	.0300
Methyl alcohol	α	.253	.251	.250	.245	.243	.240
	l	.267	.267	.268	.267	.270	.273
Ethyl alcohol	α	.243	.242	.240	.237	.234	.231
	l	.256	.258	.258	.258	.260	.262
Acetone	α	.271	.272	.273	.274	.276	.279
	l	.286	.290	.293	.299	.306	.317
Benzene	α	.220	.221	.221	.222	.222	.222
	l	.232	.236	.237	.242	.246	.252
Cyclohexane	α	.308	.307	.306	.305	.304	.303
	l	.325	.327	.328	.333	.337	.344
Cyclohexanol	α	...	...	...	.112	.113	.114
	l	...	...	...	.122	.125	.129

is the equilibrium distribution ratio of the volume concentrations of the gas in the solution and in the vapor phase. The relation between l and α is $l = \alpha T/273$, where T is the absolute temperature at which the measurement was made.

Comparison with Older Measurements.—In Tables VII, VIII and IX the results of the present measurements are compared with those of former workers. From here onward the expression solubility will always mean the Ostwald coefficient, *l*. The careful measurements of Cady, Elsey and Berger[10] of the solubility of helium in water are in good agreement with our own, but those of v. Antropoff[4] and Estreicher[11] are not. The last mentioned measurements are very uncertain for three reasons: first, the volume of gas absorbed was small in comparison with the total volume used; second, owing to the large dead space, it was often necessary to let in the gas in two portions; third, he attempted to measure the volume of gas in the dry state, which is practically impossible. V. Antropoff's measurements of the solubility of neon in water are uncertain because he used only 26 cm.^{3} of water, and of a total volume of 6.1 cm.^{3} of neon no more than 0.3 to 0.6 cm.^{3} was absorbed. The large increase of solubility with rising temperature found by v. Antropoff with neon seems improbable, when contrasted with the behavior of helium and argon.

TABLE VII

l-VALUES FOR HELIUM IN WATER

Temp., °C.	Estreicher	v. Antropoff	Cady, Elsey, Berger	Lannung
15	0.0147	0.0104	0.00933	0.0094
25	.0150	.0109	.00940	.0095
30	.0153	.0111	.00928	.0095

TABLE VIII

l-VALUES FOR NEON IN WATER

Temp., °C.	v. Antropoff	Lannung
10	0.0122	0.0117
20	.0158	.0112
30	.0175	.0110

TABLE IX

l-VALUES FOR ARGON IN WATER

Temp., °C.	Estreicher	Winkler	Lannung
10	0.0469	0.0435	0.0426
20	.0407	.0376	.0361
30	.0361	.0333	.0321

Winkler's[12] measurements of the solubility of argon in water are in fair agreement with our own, but those of Estreicher again deviate from ours. Ramsay, Collie and Travers[13] find that one volume of water at 18.2° absorbs 0.0073 volume of helium, but, as they state in the same paper that helium is insoluble in ethyl alcohol and benzene, these measurements can only have been provisional.

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

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

[12] L. W. Winkler, *ibid.*, **55**, 344 (1906).

[13] Ramsay, Collie and Travers, *J. Chem. Soc.*, **67**, 684 (1895).

Effect of Temperature on Solubilities.—As seen from the tables the solubility of each of the three gases is least in water; in the organic solvents the order of the solubilities is roughly but not exactly the same for all three gases. In each solvent helium has the smallest and argon the greatest solubility. All the solubilities are less than 0.5. In the organic solvents the solubility increases with rise of temperature and in general the more so the lower the solubility. This holds always when comparing the three gases in a given solvent and generally when comparing the various solvents for a given gas. These features can be clearly seen from Fig. 2, in which $-\log_{10} l$ is plotted against $1/T$. In this figure are included as well as our own measurements those of v. Antropoff[4] for krypton and xenon, as well as Ramstedt's[14] measurements for radon. Apart from water, whose behavior will be discussed later, in all cases straight lines are obtained and in

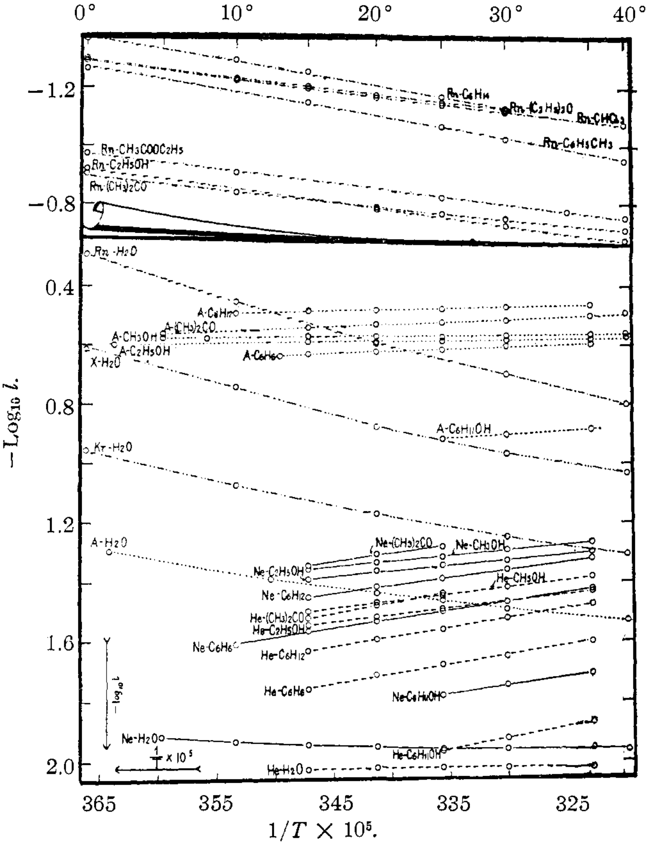

Fig. 2.—Solubility–temperature curves.

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[14] E. Ramstedt, *Le Radium*, **8**, 253 (1911), figures taken from A. Schulze, *Z. physik. Chem.*, **95**, 257 (1920).

general the higher the line the smaller the gradient. In the case of radon, where the solubility is especially high, being over 1, the gradients are negative; that is to say, the solubility decreases with increase of temperature and the more the greater the solubility. It appears that as the temperature increases, the solubility in all cases tends toward a number of the order of magnitude unity. An apparent exception to this regularity is the behavior of xenon in aniline; as its solubility is about 0.5, we should expect it to vary only slightly with the temperature; however, v. Antropoff himself admits these measurements to be uncertain.

This regularity also holds for the diatomic molecules H_2, N_2, CO and also for CO_2 in organic solvents with exception of H_2 in aniline.[15] Apparently the generally accepted idea that the solubility of gases decreases with rise of temperature is due to most measurements having been made with water as solvent, whereas it is clear from the figure that water behaves quite exceptionally as compared with organic solvents, for water as contrasted with the other solvents straight lines are not obtained. As water in liquid state is so highly associated at low temperatures, one would expect anomalies in the temperature coefficient of many of its properties; among these are its dissolving power of both monatomic and diatomic gases. De Villard[16] and De Forcrand[17] show the formation of a crystalline hydrate of argon at 0° and 150 atm. This shows the existence of strong attraction between water and argon molecules. Corresponding hydrates of neon and helium are not known and the temperature–solubility curves also deviate less from normal behavior, the solubility of helium in water being almost independent of the temperature. It seems not unlikely that there exist organic solvents, especially those with small polar molecules, whose behavior would be intermediate between normal and that of water.

From the Clapeyron–Clausius equation

$$\frac{\mathrm{d}\log_e l}{\mathrm{d}(1/T)} = \frac{u}{R}$$

where u is the heat of solution at constant volume, it is clear that straight lines in Fig. 2 denote u constant over the temperature interval in question. As already mentioned this is the case for all the solvents used except water.

Integration of this equation for constant u gives

$$\log_e l = \frac{u}{RT} + \log_e a$$

or

$$l = a\, e^{u/RT}$$

The values of u and a can be obtained directly from the slopes and intercepts on the axes of the straight lines. In Table X are given the values

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

[16] De Villard, *Compt. rend.*, **123**, 377 (1896).

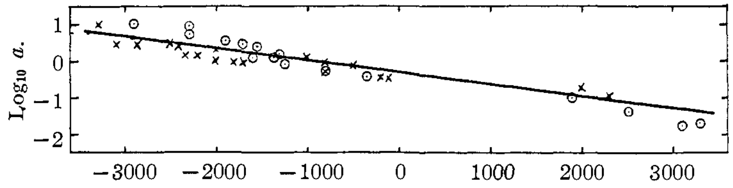
[17] De Forcrand, *ibid.*, **176**, 355 (1923).

TABLE X

VALUES OF u AND $\mathrm{Log}_{10}\,a$

Solvent		He	Ne	A	Rn	H_2	N_2	CO	CO_2
Methyl alcohol	u	−2200	−1700	− 200		−1600	−1700	−2300	3100
	$\log_{10} a$	0.15	−0.05	−0.44		0.065	0.38	0.97	−1.77
Ethyl alcohol	u	−2000	−1800	−100	2300	−1250	− 800	− 360	2500
	$\log_{10} a$	0.0	−0.03	− 0.5	−0.95	−0.07	−0.27	−0.46	− 1.4
Acetone	u	−3300	−2000	− 800	2000	−2900	−1900	−1550	3300
	$\log_{10} a$	0.97	0.29	0.05	−0.74	1.0	0.54	0.47	− 1.7
Benzene	u	−2850	−2700	−1000		−2300	−1370	−1300	1900
	$\log_{10} a$	0.42	0.49	0.12		0.58	0.06	0.17	− 1.0
Cyclohexane	u	−2850	−2400	− 500					
	$\log_{10} a$	0.42	0.39	−0.13					
Cyclohexanol	u	−3100	−2500	− 800					
	$\log_{10} a$	0.35	0.07	−0.30					
Molar latent heat of evap.		20	450	1500	4000	100	670	1400	3800

of u in calories and of $\log_{10} a$ obtained from our own measurements as well as those of Just and of Ramstedt. Values are also given for the heat of evaporation of the solutes in the pure state at their respective boiling points under a pressure of one atmosphere. The data for radon and neon are taken from Gmelin's "Handbuch der anorganischen Chemie," and the remainder from "International Critical Tables," Vol. 5. It is interesting to see that in going from helium to neon and from neon to argon the differences in the heats of solution are approximately the same as the differences in the heats of evaporation for the pure liquids.



×, 1-atomic; ⊙, 2-3-atomic.

Fig. 3.

From Fig. 3, in which $\log_{10} a$ is plotted against u, it appears that there is an approximate linear relation between them. If u is measured in calories, the relation is approximately

$$-\log_{10} a = 0.3 + \frac{u}{3000}$$

It has been suggested on theoretical grounds by Tammann[18] that a should have the value unity. As already mentioned, this suggestion is not quite in agreement with our experimental results.

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[18] G. Tammann, *Z. anorg. allgem. Chem.*, **158**, 17 (1926).

With a view to the later application of the measured solubilities to the determination of the hypothetical partition coefficients of monatomic molecules of arbitrary size, it is of importance to study the possibility of interpolation of the partition coefficients of helium, neon and argon between the various solvents. In Table XI are given the partition coefficients V and the partition exponents $\log_{10} V$ between cyclohexane and the other solvents at 25°. Cyclohexane has been chosen as standard because it is non-polar and so not associated. The partition coefficient with benzene is nearly the same for the three gases, the solubility in benzene being 30% less. The partition coefficient with cyclohexanol, which contains a polar hydroxyl group, is about 2.5, and is greatest for argon. In the remaining cases the partition coefficient also increases in the order helium, neon and argon. The differences in the partition exponents $\log_{10} V_A - \log_{10} V_{He}$ and $\log_{10} V_A - \log_{10} V_{Ne}$ are given in Cols. 4 and 5 in Table XI. They decrease in the same order as the dielectric constant, D, but there is not exact proportionality.

Table XI

Partition Coefficient and Partition Exponent (25°)

		He	Ne	A	$\log_{10} V_A/V_{He}$	$\log_{10} V_A/V_{Ne}$	D	$\frac{D}{\log_{10} V_A/V_{He}}$	$\frac{D}{\log_{10} V_A/V_{Ne}}$
Cyclohexane	V	1.31	1.25	1.37	0.0194	0.0261	2.26	116	87
Benzene	$\log_{10} V$	0.1173	0.1106	0.1367					
Cyclohexane	V	2.52	2.45	2.73	.0348	.0470	15	430	320
Cyclohexanol	$\log_{10} V$	0.4014	0.3892	0.4362					
Cyclohexane	V	0.76	0.78	1.11	.1645	.1532	21	127	140
Acetone	$\log_{10} V$	−0.1192	−0.1079	+0.0453					
Cyclohexane	V	0.86	0.895	1.29	.1761	.1588	26	147	165
Ethyl alcohol	$\log_{10} V$	−0.0655	−0.0482	0.1106					
Cyclohexane	V	0.77	0.84	1.245	.2087	.1709	31	148	181
Methyl alcohol	$\log_{10} V$	−0.1135	−0.0757	0.0952					
Cyclohexane	V	2.90	3.70	9.8	.5288	.4230	80	154	190
Water	$\log_{10} V$	0.4624	0.5682	0.9912					

The present research was carried out at the Chemical Laboratory of the Royal Veterinary and Agricultural College, Copenhagen. I am much indebted to Professor Bjerrum for his continuous interest in my work and for providing such good facilities.

Summary

1. The solubilities l, of helium, neon and argon in water, methyl alcohol, ethyl alcohol, acetone, benzene, cyclohexane and cyclohexanol were determined in the temperature interval 15 to 37°.

2. Log l varies linearly with $1/T$ for the organic solvents, but not for water.

3. In the formula $l = ae^{u/RT}$, where u is the heat of solution, it is found that for monatomic molecules, diatomic molecules and for carbon dioxide there is an approximate linear relation between log a and u.

COPENHAGEN, DENMARK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF SASKATCHEWAN]

STUDIES ON THE THERMOCHEMISTRY OF THE COMPOUNDS OCCURRING IN THE SYSTEM $CaO-Al_2O_3-SiO_2$. II. THE HEAT OF SOLUTION OF CALCIUM HYDROXIDE IN $HCl\cdot200H_2O$[1]

BY THORBERGUR THORVALDSON AND WELDON G. BROWN

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Introduction

Thomsen[2] reports two determinations of the heat of solution of hydrated lime in $HCl\cdot300H_2O$, giving the values 30.41 and 30.57 or a mean of 30.49 kg. calories per mole. The calcium hydroxide is described by Thomsen as a moist powder, 90.88 g. of the material containing 74 g. of $Ca(OH)_2$. Berthelot[3] determined the heat of solution of calcium hydroxide in water and the heat of neutralization of the solution by hydrochloric acid (1 equivalent in 2 liters). He obtained thus the value 30.96 kg. calories per mole for the heat of solution of calcium hydroxide in hydrochloric acid.

An accurate value for the heat of solution of calcium hydroxide in $HCl\cdot200H_2O$ was required in connection with the present studies. Since the two values given above differ by 1.5% and are for different concentrations of acid, it was decided to redetermine the heat of this reaction.

Apparatus and Experimental Procedure

The calorimeter was of the Richards adiabatic type, with a modification in the method of stirring which prevented diffusion or convection of air between the calorimeter and the environment. The stirrer, the Beckmann thermometers and the method of introducing the sample into the calorimeter are described in the first paper of this series.[4]

The air gap between the calorimeter can and the jacket was 6 mm. wide. A negative thermal head[5] of $0.01 \pm 0.005°$ was maintained between the outside jacket and the calorimeter. It was found that fluctuations in

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[1] The authors take pleasure in acknowledging generous financial assistance from the National Research Council of Canada.

[2] Thomsen, "Thermochemische Untersuchungen," **1883**, Vol. 3, p. 248.

[3] Berthelot, *Ann. chim. phys.*, [5] **4**, 531 (1875).

[4] Thorvaldson, Brown and Peaker, THIS JOURNAL, **51**, 2678 (1929).

[5] Thermal head: temperature of calorimeter *minus* temperature of jacket.