

55. *Solubility of Vapours in Gases.*

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THE mutual nature of solubility with regard to the two constituents of a solution is clearly seen when both solute and solvent are liquids. We do not find one liquid A extremely soluble in a second liquid B, whilst B is only slightly soluble in A.

With solutions of gases in liquids both constituents are found in the two phases, and it becomes of interest to determine if the system shows a mutual solubility between the

components in each phase such as is found for a liquid pair. For example, will a gas, such as ammonia or hydrogen chloride, which is very soluble in water, attract water into the vapour phase? In other words, will there be an attraction between the two substances in the gaseous as well as in the liquid state?

There is no recorded case of a liquid being more volatile in the presence of a gas than when it exists alone. An extensive investigation of the partial pressures of aqueous ammonia solutions (Perman, J., 1903, **83**, 1168) shows that, although ammonia is very soluble in water, yet there is a smaller concentration of water vapour in the gas phase when that liquid is confined by an atmosphere of ammonia than when the water is allowed to evaporate into a vacuous space. In a number of cases investigated by Campbell (*Trans. Faraday Soc.*, 1914, **10**, 197) it has been found that the vapour pressure of a liquid is always lowered by the presence of a gas soluble in the liquid.

This lowering of the saturated vapour pressure of a liquid in the presence of a soluble gas may be attributed, however, to the ordinary lowering of the vapour pressure caused by a solute, and does not preclude the possibility of attraction between the two constituents of the vapour phase. The existence or otherwise of such attraction may be made evident by comparing the sum of the partial pressures of the two constituents considered separately with the total pressure when the constituents are mixed. If the total pressure of the mixed gases is less than the sum of the separate pressures, then the decrease in pressure must be attributed to attraction between the two types of molecule in the gas phase. Such an attraction between gas molecules has been found for gas mixtures at high pressures; for instance, Masson and Dolley (*Proc. Roy. Soc.*, 1923, *A*, **103**, 524) found a decrease in pressure of about 8% when equal volumes of ethylene and argon or ethylene and oxygen are mixed at 100 atmospheres pressure. Similarly at atmospheric pressure, Sayce and Briscoe (J., 1929, 1302) showed that ether vapour in the presence of carbon dioxide exerts a lower pressure than when existing alone, thus indicating that a union of some sort must take place between the two types of gas molecule. Randall and Sosnick (*J. Amer. Chem. Soc.*, 1928, **50**, 967) treated the question of gaseous solutions from the thermodynamic point of view.

An attempt has now been made to determine the attraction, under ordinary conditions of temperature and pressure, between the vapours of methyl alcohol, ether, acetone, or chloroform and the gases carbon dioxide, ammonia, sulphur dioxide, or hydrogen chloride; both qualitative and quantitative methods have been employed.

EXPERIMENTAL.

In the qualitative method, which was used only in the case of methyl alcohol vapour, equal volumes of a gas and of air saturated with methyl alcohol vapour were allowed to mix, and after equilibrium had been attained the change of pressure at constant volume was observed. The following results indicate that a considerable attraction exists between hydrogen chloride and the vapour of methyl alcohol, while smaller attractions are found between the vapour and the other gases.

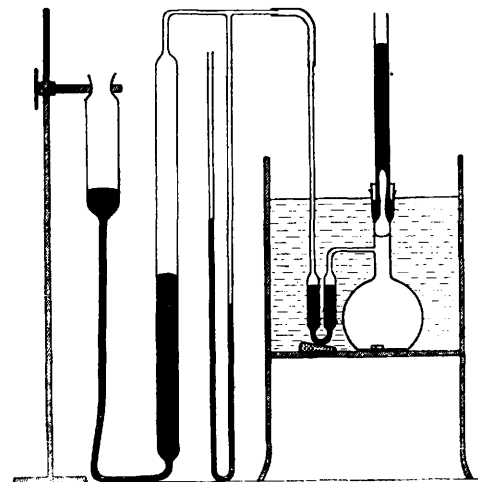
Contractions (mm. Hg) when air saturated with methyl alcohol vapour is mixed with an equal volume of a second gas at 25°.

HCl.	CO ₂ .	SO ₂ .	NH ₃ .
59, 61	1, 2	7, 8	8, 9

The quantitative apparatus (see fig.) is a modified form of that employed by Sayce and Briscoe (*loc. cit.*); it is simpler to operate but gives less accurate results. A flask of about 250 c.c. capacity is fitted with a side tube bent in the form of a U, which is filled with mercury up to an etched mark on the limb nearer the flask. The volume of the flask as far as the etched mark is determined by filling with water and weighing; it was 239.7 c.c. The ground stopper is of the form shown, and is enabled to resist a considerable pressure inside the flask by means of the deep mercury seal. This seal is formed by inserting the rubber stopper with its attached wide-bore tube into the neck of the flask (after the ground stopper has been placed in position) and filling the tube with mercury to a depth of about 20 cm. The open end of the U-tube is connected with a manometer and a pressure-regulating apparatus as shown.

In carrying out an experiment, the detached flask is first dried and the neck fitted with a

calcium chloride tube; dried gas is then passed through the U-tube to sweep the air out of the side arm. Mercury is now placed in the side tube till its level reaches the etched mark, and the flask is then placed in a glass-sided thermostat at 25° and adjusted so that the limbs of the U are vertical. The calcium chloride tube is now removed, 15 c.c. of mercury poured into the flask, the gas passed in directly for 10–20 minutes, the neck of the flask closed, and the apparatus left for about 20 minutes to acquire the temperature of the bath. Meanwhile, a Hofmann bottle containing the liquid whose vapour is being investigated is weighed. The flask is now opened and the bottle dropped on to the layer of mercury, the stopper at once inserted, and the mercury seal placed in position.



The temperature of the bath is now raised to 70° or 80° in order to vaporise the liquid, the evaporation being assisted by reducing the pressure by means of the pressure regulator. After an hour's heating, the bath temperature is again brought to 25°, and readings are taken after the lapse of two hours.

TABLE I.

	Ether ($M = 74$).			Methyl alcohol ($M = 32$).			Acetone ($M = 58$).			Chloroform ($M = 119.4$).		
	G.	Mm.	P.	G.	Mm.	P.	G.	Mm.	P.	G.	Mm.	P.
Air	0.0739	78.45	18.82	0.0332	81.05	18.93	0.0329	46.24	19.54	0.0627	42.11	19.23
	0.0738	78.45	18.84	0.0329	81.23	18.94	0.0329	46.87	19.81	0.0627	42.34	19.32
	0.0737	78.14	18.79	0.0327	81.14	19.03	0.0329	46.91	19.83	0.0625	41.53	19.01
		Mean	18.82	0.0328	80.94	18.92	0.0329	46.53	19.66	0.0621	41.40	19.08
				0.0326	81.16	19.09		Mean	19.71		Mean	19.16
CO ₂	0.0737	76.31	18.35	0.0329	76.14	17.75	0.0324	45.69	19.61	0.0624	40.96	18.82
	0.0738	76.19	18.30	0.0330	76.36	17.74	0.0330	45.15	19.02	0.0626	40.70	18.61
	0.0738	76.41	18.35	0.0327	75.66	17.74	0.0326	45.55	19.43	0.0620	40.56	18.74
		Mean	18.33	0.0323	78.05	18.54	0.0329	44.94	18.99	0.0619	40.71	18.82
				0.0327	78.99	18.53	0.0329	45.71	19.32		Mean	18.75
				0.0326	78.77	18.54		Mean	19.27			
				0.0327	79.58	18.66						
			0.0324	78.83	18.66							
				Mean	18.27							
SO ₂	0.0735	72.01	17.37	0.0328	75.53	17.66	0.0327	40.53	17.24	0.0627	40.03	18.27
	0.0737	71.95	17.30	0.0328	74.51	17.43	0.0328	41.22	17.47	0.0621	39.26	18.09
	0.0738	72.20	17.34	0.0325	74.52	17.59	0.0332	41.57	17.41	0.0625	39.62	18.14
		Mean	17.34	0.0326	74.97	17.64	0.0328	40.93	17.35		Mean	18.17
					Mean	17.58		Mean	17.37			
NH ₃	0.0738	76.13	18.28	0.0330	61.35	14.27	—	—	—	0.0623	39.42	18.11
	0.0738	76.72	18.43	0.0329	64.12	14.95	—	—	—	0.0619	39.02	18.04
	0.0739	76.03	18.24	0.0329	64.30	14.99	—	—	—	0.0623	39.13	17.98
		Mean	18.32	0.0330	64.60	15.02	—	—	—	0.0620	39.21	18.10
					Mean	14.81					Mean	18.06
HCl	0.0738	58.88	14.15	0.0325	—33.69	—7.95	0.0328	31.31	13.26	0.0620	39.84	18.40
	0.0738	58.48	14.05	0.0325	—35.44	—8.36	0.0326	28.81	12.28	0.0624	39.11	17.94
	0.0739	56.82	13.37	0.0325	—35.53	—8.39	0.0327	24.08	10.23	0.0624	38.95	17.86
		Mean	13.92	0.0325	—19.65	—4.64	0.0326	23.40	9.98	0.0627	39.50	18.03
				0.0182	—13.91	—5.86	0.0330	25.02	10.54	0.0622	39.35	18.10
					Mean	—7.04		Mean	11.26		Mean	18.07

Droplets of liquid appeared on the walls of the flask with the mixture of hydrogen chloride and methyl alcohol vapour.

In order to take the pressure readings, the level of the mercury in the U-tube is brought to the etched mark by means of the pressure-regulating apparatus, the reservoir of which is raised or lowered by means of a rack and pinion. The pressure indicated by the manometer is read

by means of a cathetometer, a series of readings being taken at 15-minute intervals during about $2\frac{1}{2}$ hours till the manometer pressure remains steady. The pressure indicated by the manometer is corrected for any change of barometric height occurring during the time of the experiment.

The results obtained are shown in Table I; col. 1 gives the weights (in g.) of liquid used, and col. 2 the corrected pressures (mm. Hg) obtained. In order to compare the different results with one another, they are calculated in col. 3 to the common basis of the pressure (P) exerted by 1 millimol. of vapour in a volume of 1000 c.c. at the temperature of the experiment. The theoretical pressure exerted by this amount of substance is 18.58 mm., it being assumed that 1 g.-mol. occupies 22,400 c.c. at *N.T.P.* It will be seen that the pressures exerted in air are all slightly greater than the theoretical, whilst in the presence of any of the other gases they are less; in mixtures of hydrogen chloride with the vapours of methyl alcohol, ether, or acetone the pressure decreases are very marked, thus indicating considerable attraction between the two constituents of the mixture.

In view of the suggestion (p. 208) that a gas which was very soluble in a liquid should show an attraction for the vapour of that liquid, the solubilities of the gases in the liquids are compared with the decrease of pressure obtained on mixing the gases with the vapours. To facilitate comparison, the solubilities are expressed as g.-mols. of dissolved gas per g.-mol. of liquid solvent. The data are given in Table II, but only for the liquids methyl alcohol and ether, as the solubilities in the other liquids have not been completely investigated. The solubilities in ether are at 15°, and those for methyl alcohol at 25°. The values were obtained by calculation from the figures given in Seidell's solubility tables; since these data were obtained by different workers and with different methods, the values can only be taken as approximate.

TABLE II.

Solubilities of gases in ether and methyl alcohol compared with the attractions between the gases and the vapours of the solvents.

	HCl.	SO ₂ .	CO ₂ .	NH ₃ .
Ether as solvent.				
Solubility	0.774	—	0.0236	0.045
Attraction	4.9	1.5	0.49	0.50
Methyl alcohol as solvent.				
Solubility	0.717	0.225	0.0064	0.376
Attraction	26.0	1.40	0.71	4.17

It will be seen that very soluble gases show great attraction for the vapours of the liquids in which they are soluble, but it cannot be said that the relation is a quantitative one.

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