

Sound Velocity in Liquid Mixtures

IN an earlier paper,¹ I proposed a relation between the velocity of sound v in liquids and its molecular volume V , viz., $v^{1/3}V = R$ where R is a constant independent of temperature. It is found that the constant R is an additive function of the chemical composition. Isomeric substances of similar constitution have the same value of R . Further the difference in R between successive members of a homologous series has a constant value independent of the type of compound. The mean difference corresponding to the value of R of the CH_2 -group has been found from the examination of several series to be 195.

The velocity of sound in mixtures of liquids has been determined by a number of investigators² either by the method of diffraction of light by sound waves of high frequency or by the Sonic Interferometer. If the values of R of solute and solvent are additive then the value of R for the mixture is simply given by

$$R_{12} = xR_1 + (1-x)R_2 \quad (1)$$

where R_1 is the value of R of the solute and R_2 that of the solvent, and R_{12} that of the mixture. x is the molar fraction of the solute. The quantity R_{12} is given by

$$R_{12} = \frac{M_{12} \cdot v_{12}^{1/3}}{\rho_{12}} \quad (2)$$

where v_{12} and ρ_{12} are the measured velocity of sound and density of the liquid mixture respectively; M_{12} is the mean molecular weight, thus $M_{12} = xM_1 + (1-x)M_2$, M_1 and M_2 being the molecular weights of the solute and solvent respectively. The value of R_{12} calculated from R_1 , R_2 and x according to equation (1) is compared with the value of R_{12} obtained from M_{12} , v_{12} and ρ_{12} according to equation (2) and it is found that the agreement is excellent. As an example the results for solutions of butyl alcohol in heptane are given in the following table:—

Equally good agreement has been obtained for solutions of benzene, carbon disulphide, ethyl acetate in carbon tetrachloride. Equation (1) can, therefore, be applied to determine the values of R_1 or R_2 from measurements of the

x	ρ_{12}	v_{12}	R_{12} acc. to (2)	R_{12} acc. to (1)
0.2570	0.7004	1139	1393	1394
0.4843	0.7252	1155	1266	1270
0.7457	0.7603	1190	1125	1128
0.8243	0.7735	1205	1084	1085
1.0000	0.8061	1245	989	..

$$R_1 = 989, R_2 = 1535.$$

velocity of sound in, and density of, solutions instead of pure liquids. If the mixture law given in equation (1) is extended to the case where the solute is a solid, it is possible to calculate the velocity of sound in solids. Details will be published very soon.

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December 11, 1940.

¹ M. Rama Rao, *Curr. Sci.*, 1939, **8**, 510; *Ind. Jour. Phy.*, 1940, **14**, 109.

² Bergmann, 'Ultrasonics and their Scientific and Technical Applications'.

Ammonia Synthesis from Active Nitrogen and Hydrogen

THE classical work of Haber,¹ Le Rossignol,² Nernst³ and numerous others has established the principal optimum conditions for the above reaction produced thermally. Under different types of electrical discharge, however, the ammonia yields are poor even when the variously mixed gases, are activated in the presence of a number of substances. The results have, however, revealed the operation of some significant factors. Anderson,⁴ for example, employing slow moving electrons has found that ammonia formation is negligible at voltages short of the ionisation potential of nitrogen; according to Lewis,⁵ a mixture of active nitrogen and atomic hydrogen is reactive; Dixon and Steiner⁷ observed ammonia with

active hydrogen and nitrogen in the presence of iron, nickel and copper.

Besides these and similar observations which are mainly of theoretical importance, no systematic and detailed information is available in the now considerable literature on active nitrogen in regard to its utilisability for ammonia synthesis. In the course of studies of its interaction produced under a variety of conditions with a wide range of substances, we have found that (i) secondary ionisation is practically the only necessary and sufficient condition for the activation of nitrogen, and that (ii) its deactivation results by the continued operation of the exciting field. Result (i) is at variance with the view adopted in some of the standard works as to the necessity of a "condensed discharge"¹; it serves, however, chiefly to increase the density of ionisation and therefore, of active nitrogen. We have found that hydrogen even in small proportions acts anticatalytically towards active nitrogen. Besides the influence of this factor, it is to be anticipated from (ii), that but small yields would follow any reaction involving active nitrogen with a *stationary* mixture of nitrogen and hydrogen under the discharge. The experimental results were in agreement with this deduction. A careful streaming of the glowing gas at an adequate pressure-gradient was of primary importance. The catalyst, selected from amongst materials found previously to be sensitive towards active nitrogen, was placed in the 'after glow' of the streaming gas. In a large number of cases nitrides were found; these gave ammonia on decomposition with hot water. This, however, changed the catalyst and necessitated its replacement from time to time. The efficiency of the process also suffered as its operation was thus discontinuous. Hydrolysis with water was therefore replaced by interacting the catalyst with hydrogen. The procedure finally adopted consisted in leading over the catalyst, a carefully regulated stream of active nitrogen followed by that of hydrogen pre-subjected to electrical discharge. The latter gas reacted with the exposed catalyst to give

ammonia directly, which was readily absorbed from the effluent gases. Ammonia yields were appreciable in the cases of magnesium, cadmium, aluminium, sulphur, chromium and monazite. They were comparatively poorer with alumina, zinc, arsenic, tungsten, nickel, selenium, tin, cobalt and calcium. A marked improvement was effected by heating to about 200° C., the catalyst and also *nitrogen before activation*.

The gases were not allowed to mix; the unused portion of either of them could therefore be used over and over again. Furthermore, the activity of any of the catalysts continued unimpaired for long periods. The chief requisite for its successful performance is, that at the working temperature, the nitride formed should be unstable and reactive towards hydrogen. This is illustrated by the fact that but negligible yields of ammonia were obtained, when silicon was employed as a catalyst; its nitride is known to be exceedingly stable and unreactive.

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¹ *Zeit. Anorg. Chem.* 1905, **43**, 111.

² *Ibid* 1908, **14**, 181.

³ *Ibid.*, 1907, **13**, 521 ; 1908, **14**, 373 ; 1910, **16**, 96.

⁴ Cf. Mellor, *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, 1924, **8**, 149-51.

⁵ *Ibid.*, p. 84; Kaplan, *Proc. Nat. Acad. Sci.*, 1928, **14**, 258; Reyleigh, *Proc. Roy. Soc.*, 1911, **85**, 219; Lowry, *Inorganic Chemistry*, 1931, p. 414; Partington, *Inorganic Chemistry*, 1933, p. 545; Willey, *Collisions of the Second Kind*, 1937, p. 19.

⁶ *J. Amer. Chem. Soc.*, 1928, **50**, 27 ; 1929, **51**, 654.

⁷ *Zeit. Physikal. Chem.*, 1931, **14**, 397.

A Light Effect in Chlorine under Electrical Discharge

THE marked adaptability of a Siemens' type, glass or silica ozoniser for the production of discharge reactions and especially for enabling