

TABLE I

	Variety	Total P_2O_5 gm./litre juice	Dialysable P_2O_5 (Effective P_2O_5)	
			P_2O_5 gm./litre	% Total P_2O_5
I (a)	CO. 312 ..	0.5350	0.5446	93.09
(b)	CO. 331 ..	0.4284	0.4149	96.85
II (a)	CO. 312 ..	0.5874	0.5754	97.96
(b)	CO. 331 ..	0.4751	0.4648	97.83
III (a)	CO. 312—			
	Top ..	0.6076	0.5861	96.46
	Bottom ..	0.8150	0.7875	96.63
	Whole ..	0.6942	0.6761	97.36
	CO. 331—			
	Top ..	0.5116	0.4984	97.42
	Bottom ..	0.7505	0.7370	98.20
	Whole ..	0.6130	0.5998	97.85

replaced by fresh distilled water daily in the initial stages and later on, on alternative days. The dialysis was continued for 7 days, with daily changes of water; all the dialysate was collected, concentrated, evaporated to dryness with a few drops of calcium acetate, ashed and the P_2O_5 estimated gravimetrically by precipi-

tation as ammonium phosphomolybdate. The results obtained with two varieties, on different dates, on the whole juice and juices from top and bottom portions are given in the table.

The above figures reveal that in the varieties examined the effective phosphate is more than 95 per cent. of the total phosphate. This is in disagreement with the results of most of the earlier workers, who obtained by their methods 50–70 per cent. of the total phosphates as possibly being available for defecation. It will also be noticed that the effective phosphate is more in the bottom juice than in the top juice. Whether these differences are common to all the Indian varieties and at different periods of growth or due to milling conditions or to defects in the methods of determination—these are factors now under investigation.

¹ Walker, H., *Ind. Eng. Chem.*, 1923, 15, 104.

² McAllep and Bomanti, *Hawaiian Planters' Record*, 26, 122.

³ Lanier, "Process," 4th Annual Conf. of Association Sug. Tech., Cuba, p. 93.

⁴ Farnell, *Int. Sug. Jour.*, 1929, p. 149.

⁵ Keane and Hill, *Ind. Eng. Chem.*, 1931, 23, 421.

⁶ Carrero, *Rept. Agric. Expt. Station*, Puerto Rico, Mayaguez, 1931, p. 11.

⁷ Beater, *Proc. South African S. Tech. Association*, 1937, p. 82.

⁸ McRae, *ibid.*, 1929, p. 54.

Chemical Reactions Involving Solids

THE structural elements of matter in a solid possess but little mobility at ordinary temperatures, compared to a fluid state, so that one would on superficial considerations even hesitate to regard solids, as such, to be involved in chemical reactions. Indeed this concept prevented for a remarkably long time any appreciable interest being taken in the chemistry of the solid state, although technical processes and particularly work on metallography had shown that under favourable conditions solids do possess a characteristic reactivity. This chemical reactivity of a solid is in particular evident when the other reacting component is a fluid, as in the combustion of carbon, reactions of graphite, reduction of oxides, etc. Reactions in which solid phases are exclusively taking part are also not uncommon: only, these cases are to be met with in different regions of chemical studies such as metallography, solid solutions, and Industrial Chemistry, and thus they escaped a general correlation. Consequently the principles underlying the reactions of solid bodies are very much less known and understood than those relating to reactions in the gaseous phase. The first important monograph on chemical reactions involving solids, "Diffusion und Chemische Reaktion in Festen Stoffen" by Prof. W. Jost, appeared in 1937. The 86th Symposium* organised by the Faraday Society in April 1938 has now helped to bring together various aspects of the subject, for a general discussion.

* *Trans. Farad. Society*, Part 8, 1938, pp. 821, 1085.

It is but natural that the general physical principles underlying these reactions should come up first for consideration. In the first two papers by N. F. Mott and J. C. Slater, the energy levels in crystal lattices, and the motion of electrons and of "positive holes" are discussed, and it is explained how the "excitation" can be transmitted over finite distances by the transfer of energy from one atom to the next. Succeeding papers deal with the conduction, diffusion, and chemical changes in solids. In the phenomena of electric conduction, and in a number of reactions involving diffusion processes, it is interesting to study the mechanism of the movement of the material ions. It is generally regarded that these movements are possible when there are deviations from the strict order of an ideal lattice. According to Wagner, some ions can exist interstitially within the normal lattice, and some positions of the normal lattice may be vacant. Motion is then possible by the jumps of the ions into the neighbouring vacant points or into the neighbouring interstitial positions. When the temperature is not too low, there is a thermodynamic equilibrium of the interstitial ions and the vacant places with the whole lattice. The energy of disorder in the ionic crystals has been discussed by W. Jost. In another interesting paper by J. D. Bernal, on the geometrical factors in reactions involving solids, it has been emphasised that the one common principle which runs through the whole field of such reactions, is the tendency to preserve crystal orientation

and atomic positions as little changed as possible.

The other contributions to this symposium, which are studies of specific reactions, are grouped as Part II and under three sections: (A) Photochemical reactions, (B) Chemical decomposition of solids (including detonation) and reactions between solid phases, and (C) Reactions of solids with gases and liquids, with particular reference to solid carbon.

Photochemical processes proceeding within the simplest of solid substances, namely, the halides of alkali metals, are of fundamental interest, and crystals of greatest chemical purity can be prepared and investigated photochemically. R. Hilsch and R. W. Pohl have proceeded further by using these crystals as solvents for substances of a similar chemical nature, and observing the photo-reactions in the latter. Thus KH in solid solution in KBr decomposes upon absorption of one light quantum ($\lambda = 228 \text{ m}\mu$), to produce a neutral K atom, and the latter is bound in a peculiar way in the lattice producing *Farbzentren*. Processes of more immediate interest in the art of photography are next considered in a series of six papers by J. Eggert, F. Weigert, C. F. Goodeve, Dr. Luppo-Cramer and others. It is essentially due to the presence of "*störstellen*" (impurities, irregular spots) in the crystal lattice, that silver bromide exhibits its photosensitiveness. This is particularly so in the region of wavelengths longer than about $500 \text{ m}\mu$. In a photo-sensitised process, which is distinguished from a direct photo-process, the essential feature is the transfer of energy from the spot where it is absorbed to one where an emission or a reaction can take place. C. F. Goodeve and J. A. Kitchner have studied the photosensitisation in solids for a number of cases. The term 'exciton' introduced by Frankel to describe the quantum after absorption by an atom, ion, or molecule, is very convenient in considering such transfer of the absorbed energy in solids. In the extreme, the 'exciton' may be a free electron, giving rise to pronounced photo-conductivity.

Equilibria of the type solid $(1) \rightleftharpoons$ solid, $(2) +$ gas have been known for a long time but a close study of these reactions has been made only recently, and particularly after the realisation of the essential interfacial character of these reactions. The reactions most closely investigated have been the dissociation of metallic carbonates, and the dehydration of solid hydrates. The formation and growth of interfaces have been studied by W. E. Garner and others. J. Zawadzki describes how various types of spurious equilibria arise in the decomposition of solids, due to sorption, and to the slow rate of crystallisation of the nuclei. The thermal decomposition of certain substances is of an explosive nature, and a study of these explosive detonations has led to the general view that they are initiated by the simultaneous decomposition of a number of neighbouring molecules in the lattice. The rate of propagation of the detonation wave in the crystal is of the order of 4000-7000 metres per second, i.e., the wave travels at about the maximum speed at which thermal vibrations could be transmitted from

one ion to another. In an aggregate of explosive material, however, W. Taylor and A. Weale regard that the decomposition follows quite a different mechanism. Here a narrow reaction zone passes through the material with velocities ranging from 1,500 to 10,000 metres per second. A very rapid decomposition takes place in this zone under the action of the impulsive forces in the pressure wave and is primarily due to the grinding together of the granules of the explosive and consequent tribochemical action.

As is well known, solid carbon exists in the three forms, diamond, graphite and amorphous carbon. The reactivity of the two latter phases is extensive and provides very interesting studies. The hexagon layer planes of the graphite crystal lattice behave as molecular entities and have properties closely resembling those of the triaryl methyls. They form layer lattice compounds such as the alkali graphites, and ferrous graphite on the one hand, and graphite monofluoride, and graphite bisulphate on the other, indicating the amphoteric nature of the hexagon layer planes. In these compounds, the hexagon layers persist and the compounds formed are ionic in nature. These reactions are naturally facilitated or hindered by the degree of accessibility of the hexagon layer surfaces. H. L. Riley finds that according to the conditions under which a carbon has been prepared, small amounts of hydrogen or hydrocarbons are present which influence the accessibility of the graphite hexagon layers to the reactant. The finely dispersed active carbons represent a distinct amorphous state according to O. Ruff, and have increased reactivity on account of the large number of lattice faults and consequent large number of free valencies. Activated carbon has found in recent years a number of varied uses. Unlike silica and alumina gels, active carbon is hydrophobic and has, therefore, the advantage that the humidity in gases and vapours which have to be treated does not effect the adsorption capacity considerably. E. Berl has reviewed the formation, properties and specifications of activated carbons.

The last group of papers deal more intimately with the reaction between oxygen and carbon. The strong free valencies on the surface of carbon due to unsaturation at the edges of the graphite crystallites, etc., hold the oxygen atoms by covalent bonds, i.e., by "chemi-sorption". Strickland-Constable puts forth the suggestion that these surface oxides of carbon are definite compounds having a considerable variety of possible structures and atomic constitutions. The kinetics of the simultaneous production of CO and CO₂ during these combustions is explained by L. Meyer and V. Sihvonen through the formation of single keto- and β -diketo groups on the boundary atomic chains of the graphite layer molecules.

There are a number of other interesting papers in this volume, of which an adequate account cannot be given here. The book as a whole is a veritable mine of useful data and informations. It is priced at 12/- with paper covers.

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