than that of the $p\sigma(s)$ group, for otherwise the energy of dissociation would decrease with excitation.

Thus it is evident that there exists a near connection between the energy states of a diatomic molecule and a triatomic one derived from it. It is also shown that atoms of the fourth family, *e.g.*, C, really undergo a tetravalent linkage from the p^4 ^3P term. This has to be considered in many questions of thermo-chemistry. A full report will be given elsewhere.

Influence of Wall Effect on the Nature of Coagulation Process.

By Dr. B. N. Desai, M.SC., PH.D.,

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IT has been realised by investigators in colloid chemistry that the walls of the containing vessel may affect the rate of coagulation. Desai (*Trans. Faraday Soc.*, **24**, 181, 1928; Patel and Desai, *ibid.*, **26**, **128**, 1930; Desai, *Kolloidchem. Beihefte*, **26**, 357, 1928; cf. Freundlich, Colloid and Capillary Chemistry—Eng. Translation—1926, p. 417) has discussed in detail the defects in the various methods used for following the course of coagulation which might be responsible for the observance or non-observance of the S-shaped coagulation velocity (C.V.) curves and the auto-catalytic nature of the coagulation process. In discussing the ultra-microscopic method it has been pointed out that the walls of the cell containing the colloid might have also some effect on the course of the coagulation reaction and that there is a possibility of greater percentage error with dilute sols— which alone can be used with this method— than with concentrated ones owing to the wall effect. In a concentrated sol the number of colloidal particles being comparatively larger than in a dilute sol, the effect of the walls in acting as centres for coalescence will be negligible.

In a recent paper S. S. Joshi and V. L. Narayan (Special Number of the *Journal of the Indian Chemical Society*, 1933, p. 41) have studied in detail the influence of wall area in the coagulation of colloidal solutions of MnO_2, Sb_2S_3 and (+ively charged) Fe_2O_3. The concentration of the disperse phase in the colloidal solutions tried by them is not very high. They have observed that the rate of coagulation is markedly increased in all cases when the wall area of the coagulating system is increased by introducing glass beads. They also find that when the same number of beads and the containing walls are paraffined, the coagulation is sensibly retarded in all cases. In the light of their results they consider unlikely that the increase in the rate of coagulation, under wall effect alone, can convert a 'slow' into a 'rapid' coagulation. They conclude that auto-catalysis cannot be considered as a general characteristic of coagulation as has been supposed by some workers, but that it is a secondary process which adds to the main course of coagulation under certain conditions.

It will not be out of place to consider in some detail the results of Joshi and Narayan in this letter as they have an important bearing on the theory of slow coagulation proposed by Freundlich (*loc. cit.*, pp. 431-447). As shown by electrosmotic, cataphoretic and stream-potentials measurements, the wall-layer of glass in contact with water becomes negatively charged. The nature of this charge will be modified considerably in the presence of electrolytes as well as when the glass surface is paraffined. It is, therefore, certain that the glass surface will help or retard the coagulation according to the nature of the charge on it and on the colloidal particles. Moreover glass walls themselves, whether paraffined or not and whether charged or uncharged, will act as centres for coalescence. In view of these considerations, it is not justifiable to say that the results of Joshi and Narayan support the conclusion that the nature of coagulation process is not intrinsically auto-catalytic.

On the other hand, their results can well be utilized to show that the nature of coagulation process is auto-catalytic. For as shown by them the walls of the containing vessel (unparaffined) make the S-shape of the C. V. curves less marked and it is quite likely that non-observance of auto-catalysis by some workers might be to a certain extent due to this effect. As shown by Desai (*loc. cit.*) the appearance of the

S-shaped C. V. curves or demonstration of the auto-catalytic nature of the coagulation process depends on the concentration of the coagulator, the purity of the sol and the concentration of the disperse phase, apart from the suitability of the method employed.


Letters to the Editor.

On the Radioactive α-Emission.

IN a recent paper (*Ind. Phys. Math. Jour.*, 1932) we have derived a wave-statistical expression for the damping coefficient of the phase space. In the above paper we assumed this coefficient to be identical with the disintegration constant for the α-particle. Later investigations of the authors, which are not yet published, show that the previous assumption is not justified. The disintegration constant is, however, related to the damping coefficient. It is shown that the constants are :

$$\lambda_{\text{damp.}} = -\frac{1}{N}\frac{dN}{dt} = \frac{\cdot 61}{h}\sqrt{U_o E}$$
$$[cf.\ \text{Eq. (36) L.C.}] \quad .. \quad (1)$$

$$\lambda_{\text{dis.}} = -\frac{1}{N_a}\cdot\frac{dN_a}{dt} \quad .. \quad .. \quad (2)$$

where N is the total number of α-particles inside the hard core and N_a the effective number present in a thin spherical shell just inside the core. It is evident that $\frac{dN}{dt} = \frac{dN_a}{dt}$.
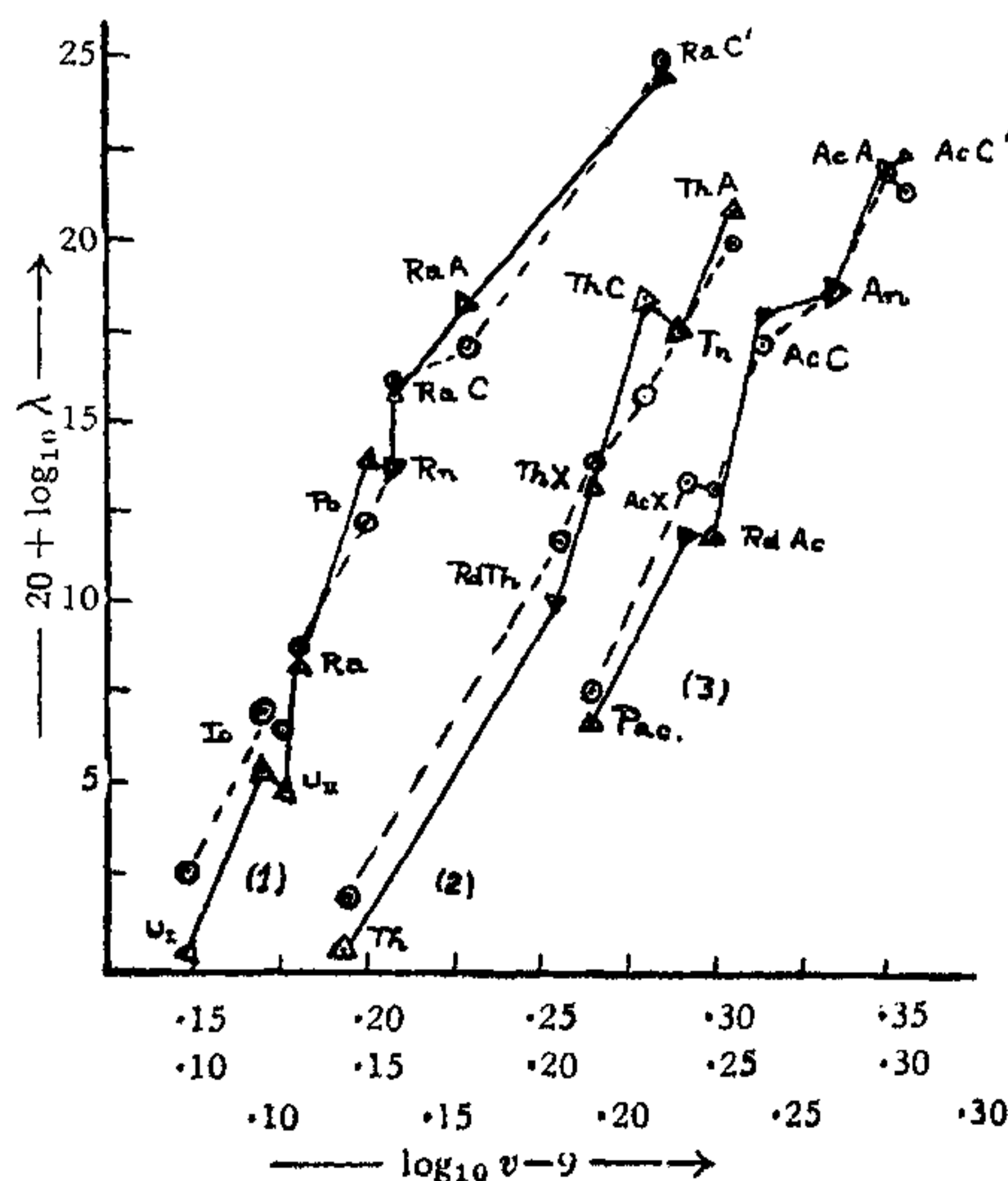
Applying the solution to the shell and using the ·boundary condition one readily obtains [*vide* Eq. (24) L.C.]

$$\frac{N_a}{N} = \text{const. cot } u_o\, e^{2k\,(2u_o - \sin 2u_o)}\, r_o^2\,\triangle r_o \quad (3)$$

Combining (1), (2) and (3) we get

$$\lambda_{\text{dis.}} = \text{const.}\ \frac{\sqrt{E}}{r_o\,h\,\cot u_o}\,e^{-2k(2u_o - \sin 2u_o)} \quad (4)$$

The theoretical values of $\lambda_{\text{dis.}}$ calculated from the above equation closely agree with the standard experimental values for the three families of radioactive substances. This is evident from the graphs where the curves drawn continuous give the theoretical values.

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A. GANGULI.

Physical Research Laboratory,
Presidency College, Calcutta,
May, 1933.

On the Two Dimensional Statistics of Kar-Mazumdar.

IN a recent paper Kar and Mazumdar (*Zeit. f. Phy.*, **55**, pp. 546–554, 1929) have obtained the distribution functions of Bose-Einstein and Fermi by generalising Gibbs' statistics. In doing so, they have introduced, over and above the free energy ψ per molecule, a new class of free energy ψ_s per 's' type cell. Thus, according to them, the total free energy of all the cells is

$$\sum_s A_s\,\psi_s = \Psi_2 \quad .. \quad .. \quad (1)$$

'A_s' being the total number of 's' type cells.

Now, as the extension of the old statistics is ultimately due to the structure of the phase space, Ψ_2 may be taken also as the additional free energy of N molecules arising out of the cells. Therefore, the total free energy is

$$\Psi = \Psi_1 + \Psi_2 \quad .. \quad .. \quad (2)$$

where $\Psi_1 = N\psi$, the classical value of the total free energy.

According to the classical statistics,

$$-\frac{d\Psi_1}{dV} = P_{(\text{mol})} = \frac{NKT}{V} \quad .. \quad .. \quad (3)$$