

## LETTERS TO THE EDITOR

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## EFFECT OF TEMPERATURE ON THE DISSOCIATION OF STRONG ELECTROLYTES BY RAMAN EFFECT

THE temperature dependence of the extent of dissociation of some strong electrolytes is studied by comparing the intensities of the Raman lines characteristic of the ions and the undissociated molecules in the Raman spectra of these substances at different temperatures. It is well known that the Raman lines of frequencies 910, 980 and 1045 in the Raman spectra of solutions of  $H_2SO_4$  are characteristic of  $H_2SO_4$  molecules,  $SO_4$  and  $HSO_4$  ions respectively, while  $HNO_3$  molecule and  $NO_3$  ion in solutions of nitric acid are represented by the Raman lines 1300 and 1040 and  $IO_3$  ion and  $HIO_3$  molecule give rise to Raman lines of frequencies 810 and 825. The following observations are made regarding the change in the relative intensities of these lines with increase of temperature.

(1) In all the cases dealt with in the present investigation, it is found invariably that on increasing the temperature, the lines characteristic of the ions decrease in intensity compared to those representing the undissociat-

ed molecules, thereby showing that the dissociation of these substances decreases with temperature.

(2) On examining the intensities of the lines characteristic of  $HNO_3$ ,  $NO_3$ ,  $H_2SO_4$  and  $HSO_4$  in solutions of nitric and sulphuric acids, it is found that the decrease in the intensity of the lines representing the ions compared to those characteristic of the undissociated molecules is less conspicuous as the concentration of the solution is decreased, thereby indicating that the rate of decrease of dissociation with temperature is *smaller* as the solution is diluted.

(3) But in the case of dissociation of  $HSO_4$  into H and  $SO_4$  in solutions of dilute sulphuric acid and bisulphates, and of  $HIO_3$  into H and  $IO_3$  in solutions of iodic acid, investigations similar to those made in (2) revealed that the rate of decrease of dissociation with temperature is *larger* as the solution is diluted.

It may also be observed in this connection that the substances referred to in (2) rapidly dissociate with addition of water, while those in (3) dissociate very slowly and are found to contain undissociated molecules even in very

dilute solutions, as described in the previous papers published by the author.<sup>1,2,3</sup>

More work is in progress to arrive at an explanation of the above results.

N. RAJESWARA RAO.

Andhra University,  
Guntur,  
September 9, 1942.

<sup>1</sup> N. R. Rao, *Ind. Journ. Phys.*, 1940, **14**, 143.

<sup>2</sup> —, *Ibid.*, 1941, **15**, 185.

<sup>3</sup> —, *Ibid.*, 1942, **16**, 71.

### DARCY'S LAW AND UPWARD MOVEMENT OF WATER IN SOIL

IN an interesting paper Ramdas and Malik<sup>1</sup> give an account of their recent studies on the upward movement of water and salt solutions in the black cotton soil. The rate of ascent of water in vertical glass tubes packed with soil was determined. The rate of ascent is at first rapid and then gradually falls off with time.

It seems worthwhile to point out in this connection that the relation between  $h$  and  $t$ , where  $h$  denotes the height upto which water rises in the tube in time  $t$ , can be immediately derived by an obvious application of Darcy's Law governing the flow of a fluid in a porous medium and the experiments of Ramdas and Malik can be used to find the permeability coefficient of the soil. Let  $h_0$  denote the maximum height to which water rises in the tube (i.e.,  $h \rightarrow h_0$  as  $t \rightarrow \infty$ ), then the pressure forcing the water upwards at time  $t$ , when the height of the water level in the tube is  $h$ , will be  $(h_0 - h)g\rho$ ,  $\rho$  being the density of water. Hence according to Darcy's Law the velocity  $v$  of flow will be given by

$$v = \frac{dh}{dt} = \frac{K}{\mu} \frac{(h_0 - h) g \rho}{h}, \quad (1)$$

$$\text{or } t = \frac{\mu h_0}{Kg\rho} \left\{ \log \frac{h_0}{h_0 - h} - \frac{h}{h_0} \right\}, \quad (2)$$

where  $K$  is called the permeability coefficient, and  $\mu$  is the viscosity of water. (It may be noted that for the flow of water in a capillary tube of radius  $a$ ,  $K$  will be  $\frac{a^2}{8}$ ). The experimental curve of Ramdas and Malik agrees with

the relation (2) for  $K = (4.68 \pm 5)$  milli-Darcys. These experiments, therefore, provide a method for determining the permeability coefficient of soils.

D. S. KOTHARI.

F. C. AULUCK.

Department of Physics,  
University of Delhi,  
November 13, 1942.

<sup>1</sup> L. A. Ramdas and A. K. Malik, *Proc. Ind. Acad. of Sci.*, 1942, **16**, 1.

<sup>2</sup> Musket, *The Flow of Homogeneous Fluids through Porous Media*, Chapter II (McGraw Hill, 1937).

### COEFFICIENT OF EXPANSION OF SOLIDS

THE model of the solid body which is the basis of the atomic heat theories of Einstein, Debye and Born-Karman is highly idealised. This idealised solid body has, as is easily seen, a zero coefficient of expansion. In order to explain the expansion of a solid, Debye assumed a law of force involving higher powers of the variation of the atomic distance. This extension gives the law deduced by Gruneisen<sup>1</sup> that at sufficiently low temperatures the coefficient of thermal expansion  $\alpha$  is proportional to the specific heat  $C_v$ .

The coefficient of volume expansion  $\alpha$  is given by the relation

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \beta_\theta \left( \frac{\partial}{\partial V} \right)_T \int_0^T C_v \frac{dT}{T}.$$

If we assume that  $C_v$  is a function of  $\frac{\Theta}{T}$ , where  $\Theta = \frac{h\nu}{k}$  after Debye or Einstein, then

$$\begin{aligned} \alpha &= - \frac{\beta_\theta}{V} \frac{\partial \log \Theta}{\partial \log V} C_v \\ &= \frac{\beta_\theta}{V} C_v \gamma, \end{aligned}$$

where  $\beta_\theta =$  isothermal compressibility

$$\gamma = - \frac{\partial \log \Theta}{\partial \log V}.$$

It is well known that the Debye formula fails to represent the specific heat curves correctly in several cases. Elaborate hypothesis have been put forward to explain away these failures. According to Raman<sup>2</sup> the vibration