

tertiary amines, and in particular pyridine, the main reaction other than quaternary salt formation appears to be the removal of halogen acid, although rearrangement of the quaternary salt to alkyl pyridine hydrohalides has not been excluded. We have used direct titration with standard alkali to determine the extent of elimination of hydrogen halide and have followed the rate of this reaction for a number of alkyl halides. We hope to be able to publish our results shortly.

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### CALCULATIONS ON THE VELOCITY OF SOUND IN NITROGEN TETROXIDE

Sir:

In a recent publication, Kistiakowsky and Richards<sup>1</sup> describe an attempt to determine the velocity of the dissociation of nitrogen tetroxide from measurements of the velocity of sound in the gas at 25° and various pressures. Their experimental curve for the change in velocity with pressure is not in good agreement with that calculated from the equation of Einstein<sup>2</sup> giving the velocity of sound in a dissociating gas at frequencies below the critical frequency. Kistiakowsky and Richards attribute the deviation to the inaccuracy of the dissociation data of Bodenstein<sup>3</sup> used in the calculations.

In a forthcoming publication, we report new data on the dissociation of nitrogen tetroxide; we have substituted these data in the theoretical equation and compared the result with the curves of Kistiakowsky and Richards. Einstein's derivation assumes that the gas in question is a perfect gas; this is obviously not true for nitrogen tetroxide. Since we have the pressure coefficient of the equilibrium constant, which varies at 25° according to the equation

$$K_p = 0.1426 - 0.7588 C_{\text{N}_2\text{O}_4}^0$$

where

$$C_{\text{N}_2\text{O}_4}^0 = \frac{\text{weight of } (\text{N}_2\text{O}_4 + \text{NO}_2)}{92.02}$$

we can calculate, for any given pressure, the deviation from the ideal condition. Further, from our extrapolation to zero pressure, we have a new value for the heat of dissociation—13,960 calories per mole at constant volume. In making the calculations, we have accepted the values assumed by Kistiakowsky and Richards for the specific heats of nitrogen tetroxide and nitrogen dioxide.

We have plotted the velocity of sound,  $V_{\text{theoretical}}$ , as calculated from

<sup>1</sup> Kistiakowsky and Richards, *THIS JOURNAL*, **52**, 4661 (1930)

<sup>2</sup> Einstein, *Sitzb. Berl. Akad.*, 380 (1920).

<sup>3</sup> Bodenstein, *Z. physik. Chem.*, **100**, 68 (1922).

our dissociation data, on a graph similar to that given by Kistiakowsky and Richards on page 4666 (Reference 1). The differences between this curve and the curve representing the direct experimental measurements of Kistiakowsky and Richards  $V_{\text{experimental}}$  are given in the second column of the following table. In the last column are given the differences based on Bodenstein's data without the pressure corrections for the equilibrium constant.

Pressure in mm.	$V_{\text{experimental}} - V_{\text{theoretical}}$ (in meters/sec.)	
	Verhoek and Daniels	Bodenstein
200	2.9	2.2
300	3.0	1.2
400	2.9	0.7
500	2.4	.1
600	1.9	-.3
700	1.5	-.7

While the agreement between the experimental curve and the theoretical curve can hardly be said to be any better using our data, the deviation is nearly constant, and the calculated velocity is always less than the observed velocity. This fact seems to indicate some constant error, either in theory or experiment. In the derivation of Einstein it is assumed that the gas is only slightly absorbing and that the dissociation proceeds according to a unimolecular reaction. It is possible that these assumptions are not sufficiently well satisfied.

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## NEW BOOKS

**Periodisches System. Geschichte und Theorie.** (Periodic System: History and Theory.) By DR. EUGEN RABINOWITSCH, Göttingen, and DR. ERICH THILO, Berlin. Verlag von Ferdinand Enke, Stuttgart, Germany, 1930. xii + 302 pp. 50 figs. 16.5 × 24.5 cm.

This is a textbook which takes up the periodic system both from a chemical and physical point of view. It is a welcome addition to our list of textbooks as it collects in one place a considerable amount of related material of great importance to the chemist who is at all interested in theoretical things, and which, as far as the reviewer is aware, has not previously all been brought together in one place in textbook form. It is to be recommended for advanced students of chemistry who wish to (or ought to) learn something about quantum theory (even though it be mostly old quantum theory) and its applications, without wading through too much material of a highly mathematical character. But many people to whom most of the material is already familiar will undoubtedly be glad to find it