

Raman Spectrum of Acetylene

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Answer to a Criticism by Moelwyn-Hughes of a Paper by Wynne-Jones and Eyring

The preceding criticism by Moelwyn-Hughes is without foundation. In defining the entropy of activation a standard state must be chosen. We chose as our standard concentration the same unit concentration used in defining the experimental reaction rate k_{exp} . We indicated this explicitly by our Eq. (4)

$$k_{\text{exp}} = \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \exp\left(\frac{\Delta S^\ddagger}{R}\right) \cdot \frac{kT}{h}$$

from which we calculate ΔS^\ddagger . This choice of the concentration of the standard state was made to avoid the volume factor

$$(V/V^\ddagger)^{n-1} = e^{R \ln (V/V^\ddagger)^{n-1}/R} \quad (5)$$

on the right side of (4) which must be included if we choose different standard concentrations for k_{exp} and for ΔS^\ddagger . Here V/V^\ddagger is the volume containing a mole at the standard concentration for k_{exp} , divided by the volume containing a mole at the standard state chosen for ΔS^\ddagger . By choosing as our standard concentration for defining ΔS^\ddagger the same standard concentration used for k_{exp} the factor V/V^\ddagger thus becomes unity and disappears from our equation (see (4)). n is the order of the reaction. Having adopted this convention for ΔS^\ddagger if we now wish to compare it with the change in entropy, ΔS , for some equilibrium in which the standard volume containing a mole is V we must (as we in fact did) first add to ΔS the term $R \ln (V/V^\ddagger)^{n-1}$. If Moelwyn-Hughes does not like this convention that is of course his privilege but no question of fact or error is involved.

HENRY EYRING
W. F. K. WYNNE-JONES

Princeton University,
November 1, 1935.

Raman Spectrum of Acetylene

In a recent issue of the *Journal of Chemical Physics*, Glockler and Morrell¹ have reported six frequencies (382, 618, 631, 1762, 1959 and 3338) in the Raman spectrum of liquid acetylene and only two (1974 and 3374) in that of the gas. With a view to explain the larger number of frequencies in the former case, they have suggested that the acetylene molecule in the liquid may be regarded as nonlinear. In this connection, we wish to point out that a particularly intense Raman spectrum of acetylene gas has been obtained by us and the frequencies observed are 589, 646, 1973 and 3371. The spectrum can be quite satisfactorily explained in terms of Placzek's selection rules. 589 and 646 are the peaks of the unresolved P and R branches accompanying the Raman active δ oscillation at 614. The corresponding Q branch is missing as may be expected. 1973 and 3371 are the well-known Raman active valency oscillations. The corresponding frequencies in liquid acetylene may easily be recognized in the numbers given by Glockler and Morrell. Besides these, the above authors have evidently observed two Raman lines at

22,556 and 21,176 cm^{-1} , respectively, and have attributed them to $\lambda 4358$. They thus obtain two new frequencies 382 and 1762. These lines have also been recorded by us in the gas and a casual examination of the picture is enough to show that they are merely the valency vibrations arising from the mercury line $\lambda 4077$ which has a wave number 24,516. The two new lines of Glockler and Morrell will then give shifts of 1960 and 3340 which are in good agreement with their own values in the liquid state. There is no necessity of assuming a bent structure at all. The detailed interpretation of the Raman spectrum of acetylene is given by us in a paper which is to appear shortly in the *Proceedings of the Indian Academy of Sciences*.

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Waltair (India),
February 19, 1936.

¹ Glockler and Morrell, *J. Chem. Phys.* **4**, 15 (1936).

The Formation of Hydrogen Peroxide in the Electrodeless Discharge in Water Vapor

Rodebush and Wahl¹ suggested that the formation of hydrogen peroxide in water vapor, which has been dissociated in the electrodeless discharge, might take place in part by a homogeneous bimolecular reaction. They pointed out that they had no direct evidence for this conclusion, but were inclined to the idea because of the conclusion of Bonhoeffer² that the hydroxyl radical had a very short life and also because the yield appeared to be independent of the length of time required for the hydroxyl to reach the liquid-air trap. Oldenberg³ has since shown that Bonhoeffer's conclusion is incorrect, and has pointed out that the chief argument in favor of the homogeneous mechanism is, therefore, invalidated.

Recently the writers have been able to demonstrate that the reaction takes place entirely in the liquid-air trap, at least, under some conditions. When a trap cooled with a dry ice and acetone mixture is placed in front of the liquid-air trap, no hydrogen peroxide and, in some cases, very little water is condensed, although it is easily demonstrated that either substance, if present, would be condensed in the trap cooled with dry ice. The usual quantity of hydrogen peroxide and water is obtained in the liquid-air trap, regardless of whether the dry ice trap is interposed or not.

It is apparent that the dissociation of the water is more nearly complete than had been assumed. These results raise a number of questions which can only be answered by further investigation. It must be admitted that we still know very little about the chemical behavior of the hydroxyl radical.

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University of Illinois,
Urbana, Illinois,
February 24, 1936.

¹ Rodebush and Wahl, *J. Chem. Phys.* **1**, 696 (1933).

² Bonhoeffer, *Zeits. f. physik. Chemie* **143**, 2 (1931).

³ Oldenberg, *J. Chem. Phys.* **3**, 266 (1935).