Dissociation Energies of Nitrogen and Nitric Oxide
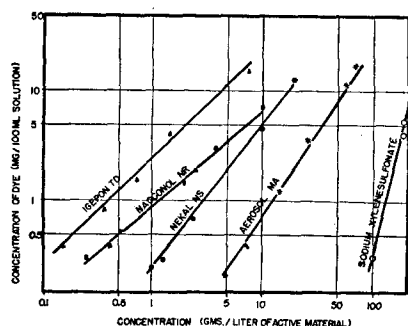
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FIG. 1. Solubilization of 1-o-tolylazo-2-naphthol in aqueous solutions containing surface-active agents. Interaction: 15 min. at 50°C.

In our investigation, first a study was made in order to determine the rate of solubilization of water-insoluble azo dyestuffs under various experimental conditions. It was found that solubilization values sufficiently close to the equilibrium values could be attained within 15 minutes if the tests were made at 50°C and if the amounts of dye solubilized did not exceed certain limits. Subsequently, it was possible to work out a practical procedure which is reproducible and rapid and can be used for the routine evaluation and classification of different types of surface-active agents by dye solubilization.

A new method of presenting solubilization data proved useful; it consists of plotting the logarithm of the amount of dyestuff solubilized against the logarithm of the amount of surface-active agent in solution. Figure 1 shows the results obtained with 1-o-tolylazo-2-naphthol solubilized in solutions of the following commercial surface-active agents in distilled water:

Detergents—Igepon *TD* (General Aniline & Film Corporation); Nacconol *NR* (National Aniline & Chemical Company).

Wetting Agents—Aerosol *MA* (American Cyanamid & Chemical Company); Nekal *NS* (General Aniline & Film Corporation).

Hydrotropic Agent—Sodium Xylenesulfonate (Wyandotte Chemicals Corporation).

The values were obtained by admixing 100 mg crystallized dyestuff with 20 ml of each detergent solution contained in a test tube and pre-heated to 50°C in a constant temperature bath. After 15 minutes of interaction in the same bath, the solutions were filtered using No. 50 Whatman paper. The filtrates, as such, or after suitable dilution, were measured in a Fisher Electrophotometer in order to determine the amount of solubilized dye. Conventional standardization and calibration procedures were employed for this determination.

As can be seen in Fig. 1, characteristic solubilization isotherms for the different types of surface-active agents (each varying in concentration over a suitable concentration range) can be represented with good approximation by straight lines. The general equation for the isotherm is $S = Kc^n$ or $\log S = n \log c + \log K$ where S is the amount of

dye solubilized (mg/100 ml of solution), c the concentration of detergent solution (grams/liter of active ingredient) and where K and n are constants which are characteristic for each solubilizing agent.

The procedure described makes possible the ready comparison of different surface-active agents. Useful and generally significant values can be obtained by determining the amount of surface-active agent required for solubilizing a certain amount, say 1 mg of dyestuff. Further details and other applications of the method will be published elsewhere.

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Dissociation Energies of Nitrogen and Nitric Oxide

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June 30, 1948

IN a recent publication Glockler[1-3] has concluded from some semi-empirical relationships that $D(N_2) = 9.764$ ev and $D(NO) = 6.49$ ev. This is also the conclusion arrived at by Gaydon[4] through a rigorous application of the non-crossing rule in interpreting the band spectra of these molecules. It is the purpose of this letter to point out that these conclusions cannot account for an experimentally determined dissociation limit in NO^+ which is as well established as any determined by the electron impact method and which cannot be circumvented by the assumption of initial kinetic energy of the dissociation products as suggested by Gaydon and Glockler.

For N^+ ions from N_2 and from NO both the appearance potential *and* the initial kinetic energy have been measured with a mass spectrometer and with a retarding potential apparatus.[5-7] Both methods agree that N^+ ions of zero initial kinetic energy appear first at 24.3 ± 0.2 ev from N_2 and 21.8 ± 0.2 ev from NO. These data lead to the values $D(N_2) = 9.75$, or 7.85, or 7.37 ev, and $D(NO) = 7.25$, or 5.35, or 5.28 ev, etc., for various choices of the excitation of the products. Thus, although it is true that either of the spectroscopic values, 7.384 or 9.764 ev, proposed for $D(N_2)$ can be fitted to the electron impact results for N_2 alone, the value $D(NO) = 6.49$ ev cannot be brought into agreement with the NO result. It would thus appear that the only set of values consistent with both electron impact and band spectroscopic results are $D(N_2) = 7.384$ ev and $D(NO) = 5.30$ ev.

The electron impact data referred to above are among those few for which a determination of the initial kinetic energy has been made (H^+ from H_2, N^+ from N_2 and NO,

C+ from CO). They are not to be confused with, or treated on an equal footing with results obtained with the mass spectrometer alone (O+ from O₂), or for which the ion peak shape is anomalous (O+ from CO and NO).[5] The N+ onset potentials in NO are not confused by the fact that there are two processes for the formation of N+ ions as Gaydon suggests. The situation is entirely analogous to that found for C+ ions from CO.

It is the opinion of this writer that the electron impact experiments should carry considerably more weight than the series comparisons presented by Glockler. It is also difficult to see the justification for the rigorous use of the non-crossing rule in view of the theoretical limitations on its applicability and evidences in band spectra of its violation. Glockler, although careful to point out that the rule is not violated for NO if $D(NO) = 6.49$ ev, is apparently willing to accept values of $D(CO)$ which involve violations for CO. Considerations relating to $D(CN)$ and $D(CN-CN)$ are based on experiments which are more readily re-interpreted than the electron impact experiments. Thus the diffuse spectra observed by Hogness and Liu-Sheng[8] in cyanogen might be interpreted differently as suggested by themselves and by Gaydon, and the result of Robertson and Pease[9] depends on the acceptance of a rather involved chain mechanism for the thermal reaction of hydrogen and cyanogen. Similarly, the Born-Haber cycle given by Glockler involves a number of questionable energetic quantities.

The occasion of this letter will also be taken to discuss interpretations of electron impact work to be found in Gaydon's book[4] which appear to this writer to be in error or concerning which new evidence is now available. The appearance potential for C+ ions from CO at 22.8 ev has been determined for ions of zero initial kinetic energy so that one cannot attribute a part of this potential to un-detected kinetic energy of the products.[10] The appearance potential for O+ ions at the maximum of its kinetic energy distribution (27 ev) is not to be compared with the value for ions of zero initial kinetic energy $\left(23.5 \begin{smallmatrix}+0.0\\-0.4\end{smallmatrix} ev\right)$. The values 23.1 and 23.5 ev are not two independent appearance potentials but the experimental limits for a single one. C− cannot be the other product in the process yielding O+ from CO because C− was looked for and not found.[5]

Concerning Gaydon's remarks about O₂ it may be pointed out that only the mass spectrometric result is available for the O+ ion and there appears to exist no valid objection to the interpretation which has been given for the O+ onset potential. The potential curve of O₂+ involved in the dissociation process cannot be that of the ground state of the molecular ion as Gaydon assumes because the known r_e values of this state and the ground state of O₂ are nearly identical.

In connection with these discussions it is of interest to note the excellent agreement now obtained for the electron affinity of the oxygen atom by the method of ionization at a heated filament[11] with the electron impact result.[5, 6] The present writer has had the opportunity to look at the original electron impact data for HCl,[12] referred to by Gaydon, and has found that if the data are evaluated by

the vanishing current method rather than the now dis-credited linear extrapolation method used by Nier and Hanson, good agreement with the band spectroscopy of HCl is obtained.

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The Influence of an Electric Field on the Depolarization Factors of Raman Lines*

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(May 20, 1948)

IT has been reported that the depolarization factors of some of the Raman lines of liquids are altered by an electric field.[1] It would seem that valuable information could be obtained by a detailed and quantitative inves-tigation of this phenomena.

In order to investigate this effect two sample tubes con-taining flat brass electrodes were made. The space between the electrodes was 5 mm in one tube, and 2 mm in the other. The electric field was applied to the electrodes by means of tungsten wires sealed through the glass. The depolarization factors of the Raman lines of the sample were determined by means of a photoelectric recording spectrograph by a method which has been described previously.[2] To determine the effect of the electric field, the spectrograph was set at the Raman line under inves-tigation and the change in intensity when the electric field was applied was measured directly by the galvanometer deflection. The effect of the field on both the strong and weak component was determined.

Measurements were made on the most highly polarized lines of benzene; cyclohexane; carbon tetrachloride and chlorobenzene and also on some of the less highly polarized lines. The field strength varied somewhat but most of the trials were made with a direct field of 20,000 volts per cm and then repeated with an alternating field of 70,000 volts per cm.

In no case did the applied field produce any noticeable change. Certainly, in no case did it change the depolariza-tion factor of the highly polarized lines by more than 0.01. It is recognized that this result is in direct contradiction to the results published previously which lead one to expect a change in the depolarization factor of the order of 0.1. However, the method of measurement used here is direct and accurate and not subject to the many errors of the photographic method.

There still exists the possibility that measurable changes in the depolarization factor may occur at higher field