

# **Testing of Colloidal Solutions by Dye Solubilization**

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The explosion temperatures being extremely high, one can suppose

$$p_r = (aT^4/3) \gg p,$$

calling to mind the well known relation:

$$E_r = a T^4 v$$

and from the preceding equations one deduces, therefore, the Rankine-Hugoniot curve

$$c_v(3/a)^{\frac{1}{2}}p^{\frac{1}{2}}+(7/2)pv\cdot(1/2)pv_1-q=0$$

where  $v = (1/\rho)$ ,  $v_1 = (1/\rho_1)$ .

For numerical computations, we observe that the energy liberated from the complete fission of 1 kg U<sub>235</sub> is

$$q \approx 19.7 \cdot 10^9 \text{ kcal./kg} = 8.4 \cdot 10^{14} \text{ kg} \cdot \text{cm/kg},$$

that the specific heat of the fission products (2 fission nucleus, 2 neutrons, 92 electrons for a single  $U_{235}$  atom) can be evaluated considering the mixture as a perfect non-degenerate gas

$$c_v = \frac{3}{2}R \frac{96 \times 1000}{235} = 1,21 \text{ kcal./}^{\circ}\text{K} \cdot \text{kg}$$

=  $5.18 \cdot 10^4 \text{ kg} \cdot \text{cm}/^{\circ} \text{K} \cdot \text{kg}$ .

Assuming finally

$$a = 7.81 \cdot 10^{-21} \text{ kg/cm}^2 \, ^{\circ}\text{K}, \quad \rho_1 = 18.7 \, \text{kg/cm}^3,$$

Eq. (1) can be written

$$7,25 \cdot 10^9 p^{\frac{1}{2}} + 3,5 pv - 26,7 p - 8,40 \cdot 10^{14} = 0.$$

Supposing that, as in the case of the ordinary explosions, the stable state of the detonation process is analytically determined by the fact that, corresponding to it, the derivative ds/dv of the entropy must be taken equal to zero, one finds the values

$$p = 9.0 \cdot 10^{12} \text{ kg/cm}^2$$
,  $v = 30.3 \text{ cm}^3$ ,

from which by means of Eq. (1)

$$T = 2.4 \cdot 10^8$$
 °K,  $D = 3.3 \cdot 10^7$  cm/sec.,  $W = 1.4 \cdot 10^7$  cm/sec.

We will finally observe that the value found for the velocity D of the detonation wave is a little smaller than the value  $U\approx 2\cdot 10^8$  cm/sec. or the mean velocity of the neutrons in thermal equilibrium at the temperature  $T=2,4\cdot 10^8$  °K. The relationship between the velocities D and U is naturally determined by the mechanism from which the chain reaction takes place.

Although the preceding calculations have been established assuming some very rough hypothesis, nevertheless we believe that they can be interesting enough because they suggest a new starting point in order to attack the problem of the detonation of nuclear explosives.

<sup>1</sup> For a review see Stewart Paterson, Research 1, 221 (1948).

# An Equation of State for Gases at Extremely High Temperatures and Pressures From the Hydrodynamic Theory of Detonation

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June 23, 1948

I HAVE read the reply¹ of M. A. Cook to my criticisms² of his paper,³ and realize that I was mistaken in supposing that he regarded his first method of solution as in practice more "general" than the second. As a matter of fact, I was more concerned with his claim that such a general solution was possible even in principle. Unfortunately, I can find no ground in his reply for revising my arguments regarding either this question or the detailed method of solution, but since these arguments have already been stated it seems unprofitable merely to repeat them.

My further point regarding the method of successive approximations as compared with step-by-step integration along an  $\alpha(v_2)$  curve was largely mathematical.  $\alpha$  is of course "well-defined," but it is a question here of determining it by the solution of certain equations. If one proceeds by a stepwise method from an assumed point in the  $(v_2, \alpha)$  plane lying below Cook's curve, one does in fact derive two members of an integral family, of which Cook's curve is the envelope. This is just what one would expect on mathematical grounds. For various *physical* reasons, including that offered by Cook, it can be judged that these integral curves are on the whole unacceptable, but this did not appear to me to dispose of all interest attached to the question.

- <sup>1</sup> M. A. Cook, J. Chem. Phys. 16, 554 (1948).
- S. Paterson, J. Chem. Phys. 16, 159 (1948).
   M. A. Cook, J. Chem. Phys. 15, 518 (1947).

# Testing of Colloidal Solutions by Dve Solubilization

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June 28, 1948

EXTENSIVE studies by McBain and collaborators<sup>1-3</sup> have elucidated dye solubilization phenomena which, in turn, gave valuable information on the structure of colloidal micelles. In some of their publications<sup>2,4,5</sup> solubilization data are given for commercial surface-active agents with the implication that dye solubilization is useful in evaluating the relative efficiency of such compounds. The experimental procedure which has been used at the Stanford Laboratory appears rather tedious since it involves the attainment of equilibrium conditions requiring periods in the order of days or even weeks.

(1942).

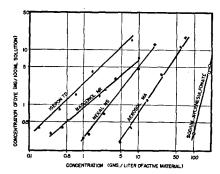


Fig. 1. Solubilization of 1-o-tolylazo-2-naphthol in aqueous solutions containing surface-active agents. Interaction: 15 min. at 50°C.

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 surfaceactive 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

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.

Present address: Institute of Textile Technology, Charlottesville, \* Present address: Institute of Action J. Am. Chem. Soc. 58, 2610 (1936).

1 J. W. McBain and M. E. L. McBain, J. Am. Chem. Soc. 58, 2610 (1936).

2 J. W. McBain, Advances in Colloid Science I (Interscience Publishers, Inc., New York, 1942), edited by E. O. Kraemer, pp. 99-142.

3 J. W. McBain, K. E. Johnson, J. Am. Chem. Soc. 66, 9 (1944).

4 J. W. McBain, A. G. Wilder, and R. C. Merrill, Jr., J. Phys. Colloid Chem. 52, 12 (1948). Chem. 52, 12 (1948).

<sup>5</sup> J. W. McBain and R. C. Merrill, Jr., Ind. Eng. Chem. 34, 915

## Dissociation Energies of Nitrogen and Nitric Oxide

HOMER D. HAGSTRUM Bell Telephone Laboratories, Murray Hill, New Jersey June 30, 1948

IN a recent publication Glockler<sup>1-3</sup> 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 Gaydon4 through a rigorous application of the noncrossing 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<sup>+</sup> ions from N<sub>2</sub> 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<sub>2</sub> 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 H2, N+ from N2 and NO,