Light Scattering in the Critical Region. II. Ethane

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Additional information on J. Chem. Phys.

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(Received November 18, 1949)

Light scattering experiments have been performed on ethane in the critical region, using apparatus and procedure previously applied to ethylene. The results are qualitatively quite similar to those obtained for ethylene, indicating that no theory so far developed completely describes the phenomenon.

USING the equipment and methods described in the previous paper, light scattering measurements were made on spectroscopically pure ethane obtained from the Phillips Petroleum Company.

Thirty-two runs were made covering densities from 0.170 to 0.234 gram per cc.[1] The results were qualitatively very similar to those obtained for ethylene. Again there appear to be four regions:

(1) A region where the λ^{-4}-law holds.
(2) A region of increasing scattering and decreasing wave-length dependence.
(3) A region of rapid decrease in scattering.
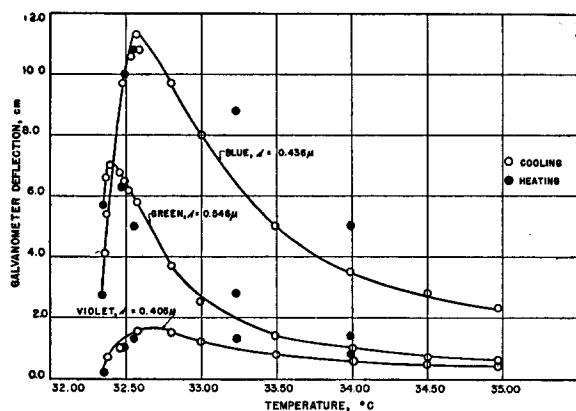(4) A region of large and erratic scattering.

The runs were reversible unless region four was entered. Typical reversible and irreversible runs are shown in Figs. 1 and 2.

The temperature of maximum scattering for the violet, blue, and green lines are shown in Fig. 3. All these maxima occur distinctly above the critical point, normally taken to be 32.28°C.

FIG. 1. Scattering as a function of temperature, reversible cycle.
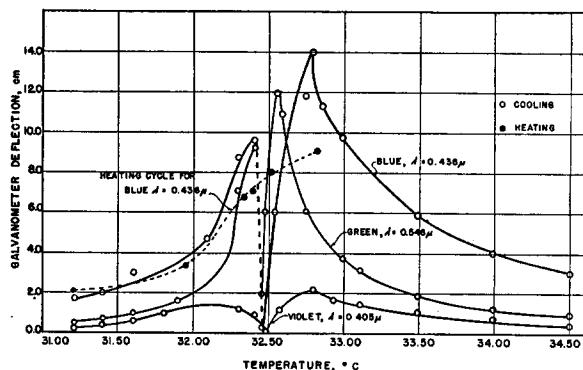
FIG. 2. Scattering as a function of temperature, irreversible cycle.
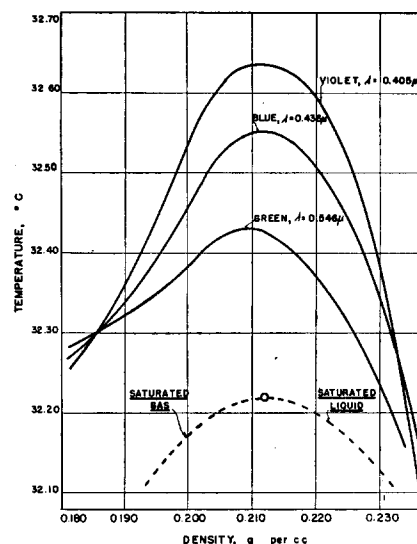

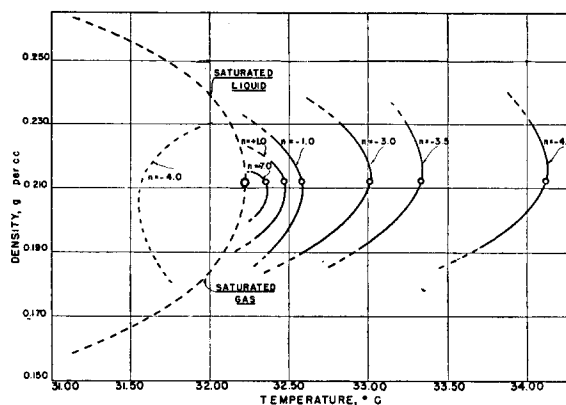FIG. 3. Temperature of maximum scattering.

FIG. 4. Dependence of scattering on wave-length.

$$\frac{\text{Corrected blue intensity}}{\text{Corrected green intensity}} = \left(\frac{\lambda_B}{\lambda_G}\right)^n$$

[1] The original data can be obtained from the M.S. thesis of A. L. Babb "Light Scattering in the Critical Phase," University of Illinois Library, 1949.
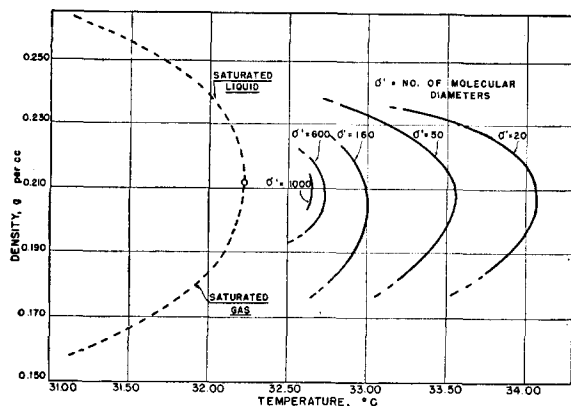
655

FIG. 5. Distance of molecular interaction or cluster diameter (expressed in molecular diameters) calculated from Ornstein and Zernike's equation. (Based on the scattering of the green and blue lines.)

The dependence of scattering on wave-length is shown in Fig. 4. In this case, runs were made far enough down into the mixed liquid-vapor phase to indicate that the λ^{-4}-law applies less than a degree below the critical point.

Cluster diameters calculated from Eq. (5) of the previous article are shown in terms of molecular diameters in Fig. 5.

From the results of those introductory works it can be seen that no theory so far developed completely describes the phenomena in the critical region. For a complete test, it will be necessary to obtain more accurate densities (in this work they were limited by the accuracy of one p.s.i. in the pressure reading) and to measure transmitted as well as scattered light. Both these refinements are being undertaken in this laboratory.

The Approximate Rate of Exchange between Iodine Atoms and Molecules

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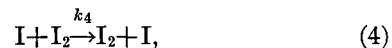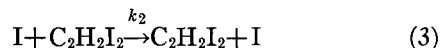(Received December 27, 1949)

The rate constant for the exchange reaction of iodine atoms with iodine molecules in hexane at 25° has been estimated by an indirect method. The rate constant is approximately 1.3×10^{-13} (atom/ml)$^{-1}$ sec.$^{-1}$ or 8×10^{10} (mole/ml)$^{-1}$ sec.$^{-1}$. The energy of activation for the exchange is probably between 2 and 3 kilocalories.

INTRODUCTION

THE exchange reactions between halide ions and halogen molecules are known to proceed rapidly. Dodson and Fowler[1] showed that bromide and iodide ions exchange completely with the corresponding halogens in less than 1 minute, and Halford[2] from a comparison of competing reactions showed that the rate constant for the formation of trichloride ion from chlorine and aqueous chloride ion lies between 6.7×10^6 and 1.7×10^{13} (mole/ml)$^{-1}$ sec.$^{-1}$. There do not appear to be any corresponding data on the isotopic exchange between halogen atoms and molecules. In fact, to our knowledge the ortho-para conversion of hydrogen[3] is the only study of the rate of exchange of a neutral atom with a diatomic molecule of the same element.

In connection with a study[4] of the exchange of iodine

atoms with *trans*-diiodoethylene in hexane solution at 25°, it became apparent that the data provided an approximate rate constant for the exchange reaction between iodine atoms and molecules. If a solution of iodine and *trans*-diiodoethylene is illuminated with visible light, the following processes take place:

$$I_2 + h\nu \rightarrow 2I \tag{1}$$

$$2I \overset{k_1}{\rightarrow} I_2 \tag{2}$$

$$I + C_2H_2I_2 \overset{k_2}{\rightarrow} C_2H_2I_2 + I \tag{3}$$

$$I + I_2 \overset{k_4}{\rightarrow} I_2 + I, \tag{4}$$

where reactions (3) and (4) represent exchanges which can be followed with the use of isotopic tracers, and the k's are rate constants (in (atom/ml)$^{-1}$ sec.$^{-1}$) for the indicated reactions. Let us adopt the following conventions:

q_a = number of quanta absorbed per ml per second,

ϕ = primary quantum yield of process (1) so defined that $\phi = 1$ corresponds to the formation of two iodine atoms for each quantum absorbed,

I = concentration of iodine atoms per ml,

* Based on a Dissertation submitted by Joseph Zimmerman to the Faculty of Pure Science of Columbia University in partial fulfillment of the requirements for the Ph.D. degree in Chemistry.

[1] R. W. Dodson and R. D. Fowler, J. Am. Chem. Soc. **61**, 1215 (1939).

[2] R. S. Halford, J. Am. Chem. Soc. **62**, 3233 (1940).

[3] K. H. Geib and P. Harteck, Zeits. f. physik. Chemie (Bodenstein Festband), 849 (1931); A. Farkas and L. Farkas, Proc. Roy. Soc. **152A**, 124 (1935).

[4] J. Zimmerman and R. M. Noyes, J. Chem. Phys. **18**, 658 (1950).