[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY, UNIVERSITY OF CALIFORNIA]

The Triple Point Temperature of Tritium Oxide[1]

BY W. M. JONES

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The triple point temperature of tritium oxide was found to be 4.49 ± 0.02°.

The value of tritium, its particular health hazard as tritium oxide, and difficulties associated with its decomposition by radioactivity made the use of a small amount of material desirable.

Preparation of Tritium Oxide.—Tritium gas, which was 99.49% T and 0.51% H according to analysis on a Consolidated-Nier mass spectrometer, was oxidized to T_2O by copper oxide. The tritium gas was contained initially in a well-outgassed bulb provided with a break-off seal and was attached to the small preparation system by means of a mercury seal standard taper joint. Provision was made to run mercury up through the single stopcock in the system to eliminate contact with stopcock grease. The 8 g. of copper oxide was contained in a 12-mm. o.d. quartz tube which was electrically heated along about 3 inches of its length. A small trap surrounded by liquid nitrogen was located as close as possible to the furnace tube exit so that the tritium oxide could be condensed as soon as possible after its formation, in order to minimize exchange effects. Prior to the preparation of the T_2O sample, the system had been baked out and then exposed to 5 successive portions of T_2. Each such portion was converted to T_2O and the water vapor allowed to be in contact with the system for several days before its removal and admission of the next portion. About 40 minutes was required for conversion of approximately 99% of the T_2 to T_2O with the CuO at 325°. The furnace was then cooled down, and the small amount of unreacted gas (some of which was He^3 formed by radioactive decay of tritium) was removed by a Toepler pump. The T_2O was then sublimed into the triple point apparatus, and the latter was sealed off. About 0.15 cc. of T_2O were prepared.

The Triple Point Temperature of Tritium Oxide.—The apparatus employed is shown in Fig. 1. The tritium oxide occupied the annular space "C" between the middle and innermost tubes. A copper–constantan thermocouple "H" of No. 40 silk-covered wires passed down through the inner tube. A thin-walled copper cap "B" fitted over and was soldered to the thin-walled Kovar tube "D" which was sealed to the end of the inner section of glass tubing. The thermocouple junction passed through a small hole in the copper cap and was then bent over. A vacuum-tight, soft solder seal was then made. A small amount of Woods metal in the bottom of the Kovar tube, covered by a little kerosene, helped to bring the thermocouple to the temperature of the surrounding T_2O. After the T_2O had been frozen into its proper location and the apparatus had been sealed off from the preparation line, the silvered jacket "A" was put on and evacuated for thermal insulation. By placing a dewar of liquid nitrogen around the jacket, the solid T_2O could be cooled by radiation to the desired starting temperature. A dewar of water was then placed around the jacket and its temperature adjusted so as to be about two degrees above the triple point temperature, which was known approximately from observations on the small portions of T_2O used in the conditioning of the preparation line. The sample warmed up partly by the energy release associated with the radioactive decay of the tritium. Thermocouple readings were made as a function of time, with a precision of 0.001–0.002°, using a White potentiometer and a sensitive galvanometer. The thermocouple was calibrated in place before and after the experiment in the region from 0 to 25° by comparison with a platinum resistance thermometer calibrated by the National Bureau of Standards. This allowed construction of a percentage deviation plot of thermocouple readings from the typical e.m.f.–temperature relationship for a copper–constantan thermocouple. The absolute error in temperature measurement should not be greater than about 0.01°.

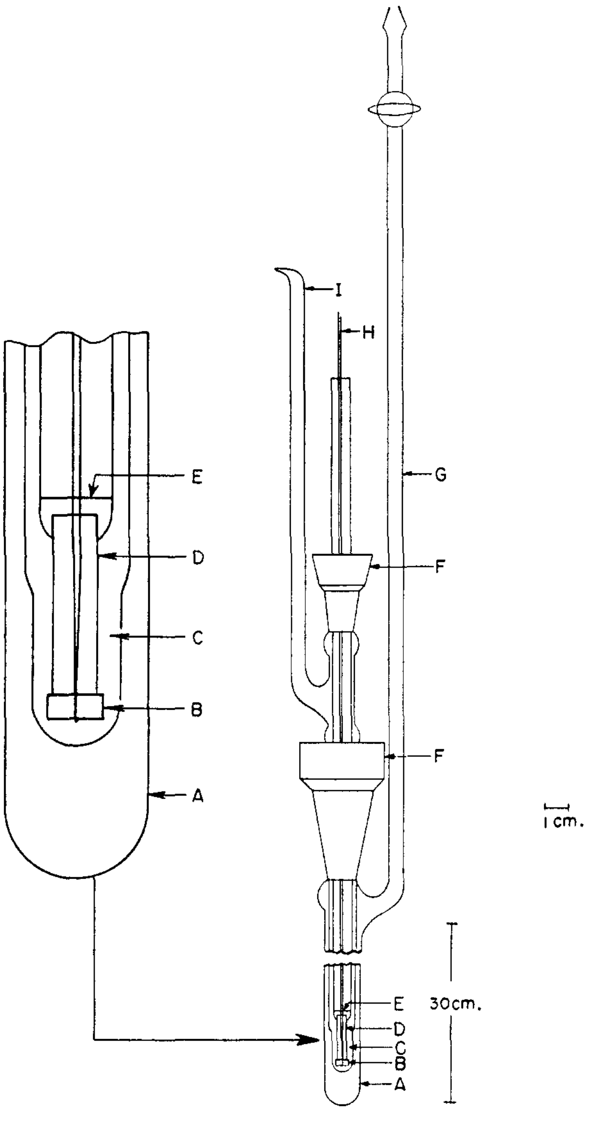

Fig. 1.—Triple point temperature apparatus: A, silvered vacuum jacket; B, copper cap; C, annular space occupied by sample; D, Kovar; E, kerosene level in inner tube; F, mercury seal standard taper ground joints; G, jacket pump-out lead; H, No. 40 copper–constantan thermocouple wires; I, sealed-off lead to T_2O preparation system. A lead provided with a break-off seal for removal of T_2O after the experiment is not shown.

After completion of the first determination, the sample was cooled down and a second determination immediately made. The material was then kept at low temperature for about 40 hours before the third determination was made. The three determinations, after correction for the small amount of hydrogen impurity, gave triple point temperatures of 4.491, 4.491 and 4.495°, respectively. The temperature–time curve in the region of interest is shown for run 3 in Fig. 2. The measurements were commenced imme-

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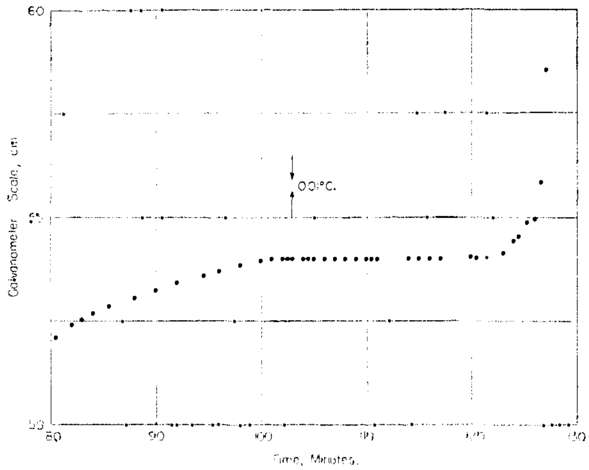

Fig. 2.—Temperature *vs.* time in triple point temperature of T_2O: Run 3.

diately after the preparation in order to minimize any small effects arising from tritium peroxide produced by the action of β-rays on the T_2O. The agreement of the three values, in spite of the presence of the material as liquid during part of the measurements, and the time lapse before the third determination, make it seem likely that such an effect is negligible. This conclusion is in accord with reasonable estimates of peroxide concentrations likely to exist, based on analyses of the decomposition gases of solid and liquid T_2O made in other connections. In correcting the observations for the hydrogen content, the percentage tritium was assumed to be 99.35. This is an average of the original composition of the gas and the composition of gas collected later from the T_2O decomposition. The corresponding uncertainty in the triple point temperature amounts to 0.007°. From the above measurements, the triple point temperature of tritium oxide is taken to be 4.49 ± 0.02°.

Prior to the measurements described above, a similar experiment was performed with deuterium, providing a test of the preparation system, particularly with regard to hydrogen contamination, as well as of the triple point apparatus. The preparation system was pretreated several times with deuterium. The triple point temperature was found to be 3.81°, in good agreement with the measurements of Taylor and Selwood[2] (3.82°), La Mer and Baker[3] (3.80°), Eucken and Schäfer[4] (3.80°), Long and Kemp[5] (3.82°), and Stokland[6] (3.813°).

The progressive increase of the triple point temperature in going from H_2O to T_2O is probably connected, at least in part, with an increasing strength of the hydrogen bonds in the solid, which is in turn to be associated with a decreasing zero point vibrational energy. This effect in the solid dominates over the oppositely acting effect in the liquid.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

A General Theory for the Gouy Diffusion Method

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Equations are derived for the light intensity distribution and the positions of intensity zeros in a Gouy diffusion fringe pattern. This treatment goes beyond previous theory for the Gouy method by using a general mathematical approach and utilizing two different methods for integrating the wave optical amplitude equation. One procedure results in a series expansion which converges rapidly for the lower fringes while the other development yields an expression converging rapidly for the central fringes. By specializing the fringe minima relation to the case of ideal diffusion, additional terms are obtained (equation (62)) for the numerical factor, $(j + {}^3/_4)$, in the interference condition of the original theory. Conditions which a cell mask must satisfy to minimize its disturbance of the Gouy fringes have been determined.

An experimental method for studying free diffusion in liquids, based on the Gouy interference phenomenon,[3,4] has recently been developed and shown to be useful either for precision determinations[5-7] or for rapid measurements.[8,9] While the original theory for this method[10] represented a good approximation to experimental conditions, its use of simple quadratic and cubic expressions to approximate the wave optical phase difference function did not allow accurate calculation of the relative fringe intensity distribution nor did it provide an estimate of the resulting error in the fringe position equations. Both of these limitations are removed in the following development which by utilizing a general series expansion for the phase difference function yields series expansions for both the fringe system intensity and the fringe position equations. The relation of the previous theory to these expansions is indicated, and a comparison between them reveals that under certain conditions the latter must be used in order to obtain accurate diffusion coefficients. In addition, the following development is not restricted to Gaussian diffusion boundaries and may be applied to any non-Gaussian symmetrical boundaries or skew boundaries for which the phase difference function is known.

The Phase Function and Amplitude Equation

In the Gouy phenomenon monochromatic light of wave length λ from a horizontal source slit S, Fig. 1, is collimated by lens U_1 and focused by lens U_2 to form a slit image in plane P. The diffusion cell, C, when filled with homogeneous liquid of refractive index n_1, Fig. 1a, has no effect on the

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