

final temperatures, a number of different determinations with different accidental reading errors are obtained in one measurement, as with the slowly changing temperatures in non-adiabatic work, and yet with the advantages of adiabatic method. The maintenance of the adiabatic condition during the slow changes of end-temperatures is very easy if the calorimeter bath is also heated electrically. Finally, it will be noted that, if the heat capacity of the calorimeter has been accurately determined, this type of measurement yields the heat of reaction directly in units of energy, the thermometer acting as an indicating instrument only—or primarily.

Summary

This paper describes a procedure, dependent upon the precise maintenance of an adiabatic condition for a few hours, whereby the relative values of all the nominal 0.01° or other minute marked intervals of thermometers may be determined to $\pm 0.0002^\circ$ or less by a continuous process, that, namely, of the generation within the calorimeter of electrical heat at a constant rate, precision of reading being secured by observations of the intervals of time during which the scale intervals are traversed. The accuracy of the method is demonstrated by data on the calibration of calorimetric mercury thermometers, and on errors of measurement which are briefly discussed.

The method is presented as the essential basis of a procedure for the complete standardization of calorimetric mercury thermometers.

Its direct applicability to thermochemical measurement is briefly discussed.

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LIGHT SCATTERING IN UNDERCOOLED BENZOPHENONE

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Introduction

The light scattering of pure liquids has been successfully described by von Smoluchowski and Einstein.¹ They have calculated from the fundamental postulate of the Boltzmann entropy-probability principle the fluctuations in density of a liquid at a given temperature, and applied to these the Clausius-Mosotti-Lorentz law which relates index of refraction n to density ρ

$$\frac{n^2 - 1}{n^2 + 2} \frac{1}{\rho} = \text{const.} \quad (1)$$

An expression emerges which gives quantitatively the relation between

¹ Von Smoluchowski, *Ann. Physik*, **25**, 205 (1908); Einstein, *ibid.*, **33**, 1275 (1910).

the intensity of light incident, I_0 , and that scattered, I_s . This may be written

$$\frac{I_s}{I_0} = kT\beta_T(n^2 - 1)^2(n^2 + 2)^2 \left[\frac{V\pi^2(1 + \cos^2 \vartheta)}{18D^2\lambda^4} \right] \quad (2)$$

where T is the absolute temperature, β_T the isothermal compressibility, k the Boltzmann constant, V the volume of liquid subjected to radiation of wave length λ , and D the distance at which the intensity I_s is measured. The angle ϑ is that between the direction of the incident light and the scattered beam.

The experimental confirmation of Equation 2, with which the names of Cabannes and Raman are chiefly associated, has been highly gratifying. A more elaborate expression of the same type has been developed which includes a factor depending on molecular anisotropy, and describes the depolarization of the scattered light. Theoretical and experimental treatment has been extended to liquid solutions near their critical mixing point, to the phenomenon of critical opalescence, and to anisotropic liquids. Hitherto, however, no experiments appear to have been made with undercooled liquids. This is probably due to the difficulty with which they may be maintained for long periods of time far below their solidification temperatures.

Recently it has been shown that, with certain liquids, prolonged undercooling is possible provided that the walls of the containing vessel, and any other adsorbents which may be present, have been wholly freed from crystals by heating the crystalline adsorbate above its melting point, which may be far above the melting point of the unbound substance.² As a result it is possible to prepare undercooled liquids which are practically permanent even far below their temperatures of solidification. One of these, benzophenone, is suitable for light scattering measurements since it melts at a convenient temperature, and may be distilled at 200° *in vacuo* without decomposition. The latter qualification is of course essential for light scattering measurements, since dust-free liquids may be obtained only by distillation.

Most of the measurements on scattered light, which have been reported to date, are based on comparison of intensities by eye. A photographic method has been used in this work because it permits the use of a spectrograph, records extremely small intensities of monochromatic light, and makes subjective error out of the question. A photographic method permits two types of measurement of light scattering. The first of these measures the absorption coefficient, h , which is defined by the expression

$$I_x = I_0 e^{-hx}$$

where I_x represents the intensity of light transmitted through a thickness x of liquid. The absorption coefficient is, therefore, compound, consisting

² Richards, *THIS JOURNAL*, 54, 479 (1932).

at any particular wave length of the sum of scattering and selective absorption losses. It is only where selective absorption is absent that deductions may be drawn from Equation 2, for when the index of refraction is very large the Clausius-Mosotti-Lorentz expression is without meaning, and the so-called "resonance scattering" appears. The absorption coefficient recommends itself highly for scattering studies on grounds of elegance: by integrating Equation 2 for all values of ϑ , the total energy of scattered light may accurately be related to the energy of the incident light and to the physical constants of the liquid. Unfortunately, however, the amount of light scattered is so small that an excessively long path is necessary and significant results were not obtained by this method. The second method of measuring the intensity of scattered light is to photograph it laterally while the liquid is intensely illuminated. Here, also, selective absorption must be absent for Equation 2 to be applicable. Since relating the intensity of the incident to the scattered beam is an exercise in photometry of considerable difficulty, and since, moreover, the quantities V , D and ϑ of Equation 2 are difficult to define experimentally, it is customary to limit an investigation of this type to the relative intensities of light scattered by two different liquids, or by the same liquid under different conditions. Since this communication deals only with the temperature dependence of monochromatic light of constant incident intensity scattered from a given liquid, Equation 2 will be used in the abbreviated form

$$I_s = T\beta_T(n^2 - 1)^2(n^2 + 2)^2A \quad (3)$$

where A is a constant. This equation is shown in the experimental section to represent the behavior of carbon tetrachloride between 20 and 55°, but to fail conspicuously in the case of undercooled benzophenone using the same apparatus and method. A test of the photographic process is also provided, in which it is found to give results of satisfactory reproducibility, but not always of rigorously quantitative significance.

Measurements

Preparation of Materials, and Source of Illumination.—The two liquids were prepared in a dust-free condition by the method of Martin,³ distillation without ebullition *in vacuo*. The carbon tetrachloride was of a guaranteed reagent grade and the benzophenone of the quality listed commercially as C. P., before distillation. The liquids were distilled into cylindrical tubes 30 cm. long and of 2.3 cm. internal diameter, which were provided on each end with sealed optical windows. A side-arm carrying a bulb was affixed to each tube to allow for thermal expansion when the cylindrical tube was completely filled. The tube enclosing the carbon tetrachloride was washed many times with dust-free distillate before finally being filled and sealed off. Since benzophenone became too viscous at room temperature to be an effective washing agent, the tube which was to contain it was first washed by water distilled *in vacuo*. It was then sealed off from the original container of water, and connected by means of a magnetic valve to the flask containing benzophenone. After evacuation the magnetic break was

³ Martin, *J. Phys. Chem.*, **24**, 478 (1920).

opened, and the benzophenone distilled with as little ebullition as possible. Since it was found impossible wholly to prevent ebullition, an elaborate series of large bulbs was arranged above the vaporizing liquid benzophenone to prevent mechanical carrying of the undistilled liquid into the receiving vessel. The resulting distillate was satisfactory in appearance, being of crystal transparency and of a very pale greenish hue. Its melting point was 48.1° , 0.4° above that of the original c. p. sample. It has remained for ten months at $20\text{--}25^{\circ}$ without crystallization.

The dust-free samples of carbon tetrachloride and benzophenone so prepared were used both for the extinction and for the scattering measurements.

Considerable attention was devoted to securing a constant source of illumination. Voltages constant over long periods of time were not available. It was necessary, therefore, to choose the source which was as nearly as possible independent of voltage. The General Electric Type S-1 bulb, which is a combination of a tungsten filament and mercury arc, was finally selected as most satisfactory for the purpose. The slight variations in line voltage which could not be prevented had at no time as much as one-half of one per cent. effect on the intensity of the mercury lines from the arc, on which conclusions are based. During long exposures these fluctuations canceled, and may be considered entirely absent. After the first few hours of running the deterioration of the lamp, even on long exposures, was negligible.

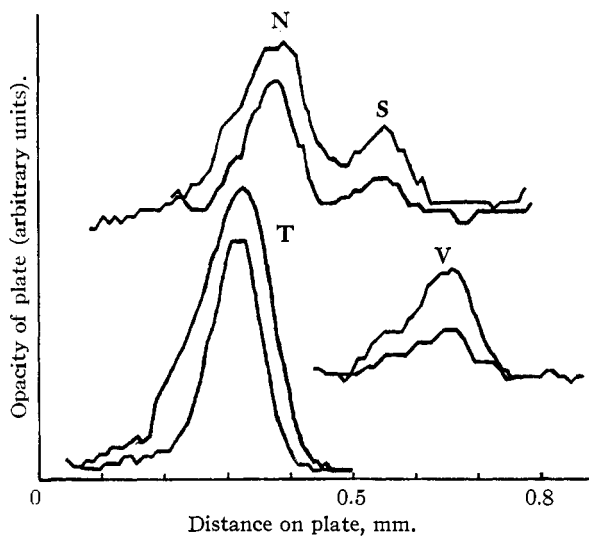
The spectroscope was of glass. It was of small aperture and about 25 cm. focus. It distributed the visible region over about 2.5 cm. of plate.

Absorption Measurements.—A few photographs were taken of the intensity of parallel light of various wave lengths transmitted through a 20.0 cm. layer of benzophenone at 20 and 70° . In the experimental arrangement the cylindrical tube described above was supported by two water-tight rubber washers, which pressed tightly against the optically flat ends of the tube, and was immersed in a thermostated cylinder containing an optically opaque solution of crystal violet in glycerin. Thus all light scattered by the liquid in the tube was absorbed by the surrounding medium. The transmitted light entered and emerged from the tube by means of small holes cut in the rubber washers, and was defined by diaphragms at suitable positions outside the tube. Exposures of varying duration through benzophenone and through Pyrex windows were taken on the same plate in order to secure adequate calibration of the plate. The photographs showed that benzophenone began to absorb strongly in the violet at about 4200 \AA . at all temperatures between 20 and 70° . Photometric analysis of the plates showed slightly greater absorption at the lower temperature, indicating a stronger scattering by undercooled than by stable liquid benzophenone, but also made clear that much longer paths must be used if results of unquestionable significance are to be obtained.

Scattering Measurements.—The apparatus used for the scattering measurements was based on that devised by Wood for photographing Raman spectra,⁴ but was modified in several respects to suit the work in hand. A brass box 20 cm. square by 30 cm. deep was provided with a thin plate glass window on one side, and pierced as close to the window as possible by two holes large enough to receive stoppers which held the scattering tube. Thus the cylindrical scattering tube was held within 0.5 cm. of the window, with about 4 cm. of each end projecting out of the box. One of these ends was painted black except for a 2-mm. diaphragm in the center of the sealed-on glass. The other was immersed in an optically absorbing solution of crystal violet in glycerin, chosen because its index of refraction is nearly that of Pyrex glass. In this way the aperture of the tube was decreased and a black background for the photographs provided. A cylindrical reflector was then placed around the 19-cm. illuminated portion of the tube. The box was finally filled with distilled water which had been boiled to remove air and main-

⁴ Wood, *Phil. Mag.*, 6, 729 (1928).

tained at constant temperature by thermostated water circulated through a long copper coil. The lamp, behind which was also an efficient reflector, was of course necessarily outside the box, being about 10 cm. removed from the axis of the scattering tube. The slit of the spectrograph was placed about 15 cm. from the diaphragm opening of the tube, and scrupulously directed down the tube's axis. The resolution of scattered light secured by this arrangement may be seen from the photometric records, Figs. 1 and 2.



N, 3650 Å.; S, 3655 Å.; T, 4047 Å.; V, 5461 Å.

Fig. 1.—Tracings of photometric records showing the light of various wave lengths scattered laterally by carbon tetrachloride at 18 and at 54°. The scattering is always less intense at the lower temperature in accordance with the Einstein-Smoluchowski theory. Logarithmic integration of these curves gave the photographic densities recorded in Table I for Plate 2.

Exposures of density suitable for photometry were obtained with carbon tetrachloride in four hours. Exposures which gave approximately equal density with benzophenone required only twenty minutes, so that if, as is customary, the light scattered laterally by ether at 20° is taken as unity, and that scattered by carbon tetrachloride at the same temperature as 1.1, the scattering factor of benzophenone is about 12. Because of the failure of the reciprocity law with photographic plates, this number must be regarded as only approximate.

In order to indicate as clearly as possible the relative intensities of scattering at two different temperatures only two strips were put on each plate, each having identical exposure times and intensities of illumination. The apparatus was wholly untouched between the two exposures except for an external adjustment of the temperature regulating mechanism and, of course, a slight movement of the plate-holder in the spectrograph. Exposures were taken on plates in alternate order as Plate 1, 20°, and then 56°, Plate 2, 56° and then 20°, etc., in order to guard against errors due to deterioration of the light source. No indications of such deterioration were found, however. The plates were developed at constant temperature by a standard procedure.

Typical photometric records of the results are given in Figs. 1 and 2, representing carbon tetrachloride and benzophenone, respectively. The greater photographic density for carbon tetrachloride at the higher temperature in accordance with Equation 2 is at once apparent to the eye. It is also apparent that no corresponding difference is obtained with benzophenone. The benzophenone photographs analyzed in Fig. 2 were those showing least divergence between the higher and lower temperatures. In all others which were photometered the difference was greater, and in the opposite direction to that predicted by the Einstein-Smoluchowski theory.

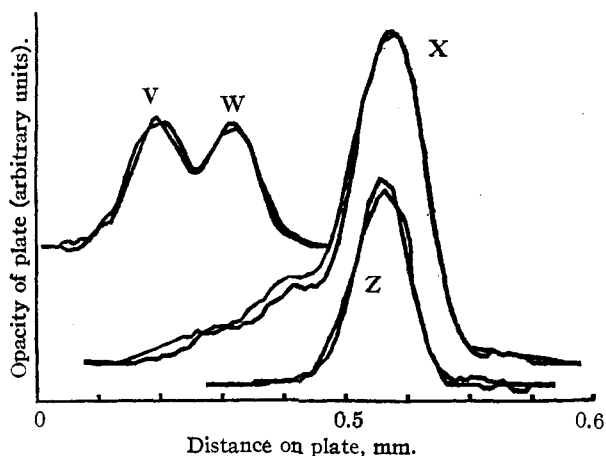


Fig. 2.—Tracings of photometric records showing the light of various wave lengths scattered laterally by benzophenone at 19 and 53°. The intensity of the two is identical within experimental error, in contradiction to the Einstein-Smoluchowski theory. Logarithmic integration of these curves gave the photographic densities recorded in Table II for Plate 3.

These records were obtained by focusing a straight-filament 4-volt lamp on the emulsion of the plate through a 10x microscopic objective, and moving the plate between this image and a Weston photronic cell. The cell, which was covered with a wide slit to eliminate scattered light and connected directly to a critically damped Leeds and Northrup Type HS galvanometer, functioned *admirably throughout*, showing no deterioration on prolonged illumination, and no zero drift. A microscopic comparator of conventional design served to give the necessary measurement of length on the plate.

The interpretation of the photometric records was based on well-known photographic practice. The photographic densities were obtained by logarithmic integration of opacity curves of the type given in Figs. 1 and 2. Since the densities to be interpreted were neither very small nor very great, the approximation

$$d = I^{lp} \quad (4)$$

where d is density, I intensity, t time of exposure and p an empirical exponent between unity and 0.8, was taken to be applicable, the validity of this approximation having been tested roughly over the range of densities considered. Since on each plate the exposure times are equal, it is obvious that at temperatures T_1 and T_2 Equations (3) and (4) may be combined to give

$$\frac{d_1}{d_2} = \frac{I_{s1}}{I_{s2}} = \frac{T_1 \beta_{T_1} (n_1^2 - 1)^2 (n_1^2 + 2)^2}{T_2 \beta_{T_2} (n_2^2 - 1)^2 (n_2^2 + 2)^2} \quad (5)$$

provided monochromatic light of constant incident intensity is used to excite the scattering.

A comparison of the intensity of scattering observed and calculated from Equation 5 is given for carbon tetrachloride in Table I, together with other pertinent data. The compressibilities of carbon tetrachloride are taken from Tyrer, and the refractive index at 20° from Landolt-Börnstein. The refractive index at other temperatures has been calculated from Equation 1, with the help of densities obtained from the "International Critical Tables." The dispersion of carbon tetrachloride has been neglected, since it introduces a factor far below experimental error. The agreement of the observed increase of scattering with that calculated is qualitatively satisfactory, but quantitatively leaves much to be desired. Lack of accuracy in the photographic method is more likely to be responsible for this than failure of the theory.

TABLE I
COMPARISON OF LIGHT SCATTERED BY CARBON TETRACHLORIDE AT TWO DIFFERENT TEMPERATURES

Refractive index for 4860 Å. at 56°, 1.444; at 20°, 1.468. Isothermal compressibility atm.⁻¹ at 56°, 1.40×10^{-4} ; at 20°, 1.05×10^{-4} .

	Exposure time, hours	Wave length, Å.	Photographic density in arbitrary units at		Observed	Calculated
			56°	20°	$\frac{I_{56} - I_{20}}{I_{20}} \times 100$	$\frac{I_{56} - I_{20}}{I_{20}} \times 100$
Plate 1	4	4358	192	131	+47	+28
	4	4046	139	108	+29	+28
Plate 2	4	4358	202	139	+45	+28
	4	4046	174	124	+40	+28

The refractive index of benzophenone has been determined at 53.5° by Auwers and Eisenlohr⁵ but its density and compressibility at various temperatures in an undercooled condition are unknown. The density was readily determined by sealing a known weight of the pure solid in a calibrated tube, heating to 150° to ensure the destruction of adsorbed crystalline nuclei, and measuring the volume, with suitable corrections for the expansion of the glass, at various temperatures. The linear relationship, where T is now in °C.

$$\rho_T = 1.132(1 - 0.00098T)$$

⁵ Auwers and Eisenlohr, *J. prakt. Chem.*, **84**, 37 (1910).

represents the density of supercooled benzophenone between 10 and 60° to better than 1%, and hence suffices for the purposes of this communication. The isothermal compressibility is not so readily accessible, and attempts to measure it by direct methods failed owing to the persistent inoculation of the undercooled liquid by nuclei from the air. It is evident, therefore, that any such measurement must be undertaken in a sealed all-glass vessel, which alone permits adequate sterilization of the liquid. An investigation of this character is outside the scope of the present communication, and the compressibility must, therefore, be estimated by an approximate relationship. It is reasonable to suppose that a large part of the increased compressibility of the liquid at higher temperatures is due to its increased specific volume. In other words, the fact that the molecules are more widely spaced at higher temperatures should make it easier to compress them. If this is the case an approximation of the type

$$\text{const.} \times \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P = \frac{1}{\beta_T} \left(\frac{\partial \beta_T}{\partial T} \right)_P$$

where v is the specific volume, might hold for all liquids. The constant is, in fact, surprisingly good considering the extreme simplicity of the assumption. For carbon tetrachloride it is 64, for carbon bisulfide 81, for benzene 63, for toluene 66 and for ethyl alcohol 73 as calculated from the data given by Freyer, Hubbard and Andrews.⁶ Water alone of the liquids compared in this way formed an important exception. The constant has been taken as 70 for benzophenone for the calculation of the percentage increase in scattering to be expected at higher temperatures according to simple fluctuation theory. Table II presents a complete analysis of two plates from densitometric records. Table III gives only the opacities of the points of maximum density of these two, and of two more plates taken under similar conditions. A comparison of corresponding points of maximum opacity with carbon tetrachloride may be made by means of Fig. 1.

It is considered that the measurements summarized in Table II establish unequivocally the irregular temperature dependence of light scattered by

TABLE II
COMPARISON OF INTENSITIES OF LIGHT SCATTERED BY BENZOPHENONE AT DIFFERENT TEMPERATURES

		Refractive index for 4860 Å. at 53°, 1.616; at 49°, 1.619; at 19°, 1.639; at 17°, 1.641. β_T/β_{19} atm. ⁻¹ at 53°, 1.214; at 49°, 1.181; at 19°, 1.00; at 17°, 0.989.				% increase obs.	% increase calcd.
Exposure time, hours	Wave length, Å.	53°	49°	19°	17°		
Plate 3	2	4358	567	...	563	...	+ 1
	2	4046	217	...	224	...	- 3
	2	5770 and 5791	260	...	269	...	- 3
Plate 6	0.5	4358	...	237	...	293	-24
	0.5	4046	...	106	...	131	-25

⁶ Freyer, Hubbard and Andrews, *THIS JOURNAL*, 51, 759 (1929).

TABLE III

MAXIMUM OPACITIES IN ARBITRARY UNITS (FULL LIGHT = 0, TOTAL DARKNESS = 3.00) READ FROM PHOTOGRAPHS OF MERCURY LINES SCATTERED BY BENZOPHENONE AT

Exposure	VARIOUS TEMPERATURES				
	T, °C.	4358 Å.	4046 Å.	5770 Å.	5791 Å.
Plate 3, 2 hours	53	2.05	1.69	1.50	1.47
	19	2.04	1.67	1.50	1.48
Plate 4, 1 hour	51	2.00	1.69	1.49	1.45
	17	2.02	1.70	1.50	1.47
Plate 5, 1 hour	54	2.00	1.56	1.35	1.33
	17	1.99	1.58	1.36	1.35
Plate 6, 0.5 hour	49	1.86	1.46	1.29	1.28
	17	1.91	1.50	1.31	1.30

undercooled benzophenone. Failure of Equation 4 may easily account for the discrepancy between measured and calculated values noted in Table I, but it cannot, at moderate light intensities, cause the reversal of the sign of the effect observed. Again, uncertainty of the compressibility coefficient as calculated from Equation 6 can cause the reversal of the sign only if the compressibility itself increases with decreasing temperature, a situation almost without precedent. The compressibility alone causes temperature variation of Equation 3, since the changes in T and n^2 almost exactly balance each other. The cause for the notable difference in temperature effect observed between Plates 3 and 6 follows as a natural consequence of the argument advanced in the next section.

Discussion

In the previous section measurements are reported which show that light scattering in undercooled benzophenone increases with decreasing temperature. Since the theory of density fluctuations in a homogeneous liquid predicts the opposite effect, it evidently cannot be applied in this case, and some constitutional difference must be assumed between undercooled benzophenone and a normal liquid. The formation of molecular aggregates, of structure between that of the crystalline state and that of the loose complexes met with in "associated" liquids above their melting temperatures, suggests itself as a reasonable explanation. These, if they are of lower energy content than the undercooled liquid, will be favored at lower temperatures. If a density change accompanies their formation, they will scatter light according to the expression developed by Lord Rayleigh⁷ for colloidal particles, which may be written

$$\frac{I_s}{I_0} = \frac{9\pi^2 N v^2}{\lambda^4 D^2} \left(\frac{n_1^2 - n_0^2}{n_1^2 + 2n_0^2} \right)^2 (1 + \cos^2 \delta) \quad (6)$$

Nv^2 here represents the product of the number and the squared volume of the scattering particles, and n_1 and n_0 refer to disperse phase and dispersion

⁷ Lord Rayleigh, *Phil. Mag.*, **47**, 375 (1899).

medium, respectively. Evidently, then, the increased light scattering which has been observed can be explained on the basis of aggregate formation only if it can be shown that the quantity Nv^2 will be increased with decreasing temperature. For this purpose it will be convenient to assign definite bounds to the volume of the aggregates, however difficult this might be to measure experimentally.

It must be emphasized at the start that the properties of undercooled benzophenone are for all practical purposes independent of time. Light scattering at 20° is equally intense whatever the previous thermal history of the undercooled liquid. The properties of the aggregates present are, therefore, undergoing reversible changes with temperature, and at a given temperature must reach a stationary condition which is subject only to thermal fluctuations. For this reason it is permissible to describe them by methods applicable only to the equilibrium state, although the undercooled liquid is of course metastable to the crystalline condition.

The free energy change accompanying the formation of a gram molecular weight of aggregates of radius r from the metastable liquid at a temperature T will be called ΔF_r . The corresponding molar heat content and entropy changes will then be ΔH_r and ΔS_r . Since

$$\Delta F_r = \Delta H_r - T\Delta S_r$$

and

$$\Delta F_r = -RT \ln \frac{p_r}{p_1}$$

where p_r and p_1 are the vapor pressures of aggregate and liquid respectively, it follows that, if the aggregate is in equilibrium with the undercooled liquid at $r = r_0$

$$\frac{p_{r_0}}{p_1} = e^{\Delta S_{r_0}/R} e^{-\Delta H_{r_0}/RT} = 1$$

and consequently that

$$\frac{\Delta S_{r_0}}{R} - \frac{\Delta H_{r_0}}{RT} = 0 \quad (7)$$

The question evidently turns, therefore, on the variation of ΔH_r and ΔS_r with r and T . ΔH_r is compound, being partly work done against the surface energy and partly that gained by liberation of what may be called the latent heat of association. If we call N_r the number of aggregates of radius r which are formed by a gram molecular weight of undercooled liquid, the heat change accompanying the substitution of an aggregate for an equal mass of undercooled liquid in the interior of the latter will be

$$\frac{\Delta H_r}{N_r} = (4\pi r^2 \sigma_r - \Delta e_r)$$

where σ_r is considered the total surface energy, and Δe_r is the energy liberated due to the orientation of the molecules in the interior of the aggregate. Since neither of these quantities will be very sensitive to tem-

perature, their variation in this respect may be neglected, and the variation of $4\pi r^2 \sigma_r - \Delta e_r$ with r alone considered. In general, since Δe_r increases with r^3 and $4\pi r^2 \sigma_r$ with r^2 , their difference will change in sign with increasing values of r , and unless σ_{r_0} is very large, ΔH_{r_1} will be negative, that is, the heat content of the aggregate will be less than that of an equal mass of undercooled liquid, for all radii not very close to molecular magnitudes.

The dependence of ΔS_r on r must now be considered. If two aggregates of radius, respectively, r_0 and r_1 such that $r_1 > r_0$ are considered, we may gain some idea of this dependence if we neglect surface energy and consider that $\Delta H_{r_0} = \Delta H_{r_1}$. In this case Boltzmann's principle may be applied, the probabilities for the existence of the two states being given by

$$\frac{P_{r_0}}{P_{r_1}} = e^{(\Delta S_{r_0} - \Delta S_{r_1})/k}$$

and it is seen that the larger radius is the less probable if, as can hardly be questioned, a loss of entropy accompanies the association of the metastable liquid. This is in agreement with what is to be expected from general considerations. Since the aggregates are of lower energy content than the metastable liquid, it is reasonable to suppose that only liquid molecules of energy lower than the average may lead to their formation. Thus a large radius becomes more probable at lower temperatures, and the value of r for which Equation 7 is satisfied increases as the average thermal energy of the system is reduced. The increased power to scatter light follows as a natural consequence.

Concerning the state of aggregation of the associated complexes, it may only be said that it must differ in some important respect from the stable crystalline lattice, for if the condition $\Delta F_{r_0} = 0$, $p_{r_0} = p_1$ is applied to a crystalline nucleus, the corresponding radius will be great enough to cause crystallization if increased by an infinitesimal amount. Thermal fluctuations would ensure this increase, and a stationary state like that described above is therefore out of the question. In so far as the scattering centers undergo reversible changes with temperature it must be concluded that the anomalous light scattering in an undercooled liquid has no direct bearing on its crystallization at low temperatures. It is perhaps most reasonable to suppose that the arrangement of molecules in the aggregates resembles that in the amorphous layers periodically adsorbed on crystals which are growing into their melts.

The rate of formation of crystal nuclei in the liquid is a problem with which this communication has no concern, since no time dependence of the intensity of light scattered has been observed. As undercooled benzophenone crystallizes readily at about -60° , it is necessary to suppose crystal nuclei present at this temperature, and no reason is apparent for doubting their existence at any other temperature below the melting point.

At a temperature near that where spontaneous crystallization becomes likely, they may well play a preponderant role in scattering by the liquid. Such a case is familiar with a glass which has become milky by partial devitrification at a uniform temperature. The time dependence of this type of scattering in a liquid of low viscosity would be an interesting study, and one likely to yield information of value concerning the kinetics of the crystallization process. Since the number of crystallites in undercooled benzophenone is inappreciable at 20° , a far lower temperature is evidently necessary to obtain results of clear significance in this respect.

A quantitative description of the temperature dependence of light scattering in undercooled liquids by means of fluctuation theory is difficult because no intimate knowledge of the nature of the aggregation taking place is at present available. In general it is by no means certain that all metastable liquids will show an increase in scattering similar to that of benzophenone below their melting temperatures. Glasses, for example, and extremely viscous liquids like glycerin, may be expected to undergo changes in molecular aggregation so slowly that the reasoning used above has no practical application. Similar behavior to that of benzophenone is rather to be expected from those liquids which show anomalous dispersion of the dielectric constant immediately above their crystallization temperatures.

We wish gratefully to acknowledge the criticism of Dr. Henry Eyring concerning the conclusions reached in this communication, and the loan of the photometric equipment by the Loomis Laboratory in Tuxedo, N. Y.

Summary

It has been demonstrated by a photographic method that the light scattered by undercooled benzophenone is greater at 20° than at 55° . This result is not to be expected from the Einstein-Smoluchowski theory of fluctuations in a homogeneous medium. The hypothesis is advanced that molecular aggregates are present in the undercooled liquid which increase in number and magnitude as the temperature is lowered. It is pointed out that this is energetically possible without crystallization of the liquid, provided that the aggregates are not crystalline in character.

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