

Determination of the Adiabatic Piezo-Optic Coefficient of Liquids

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Determination of the adiabatic piezo-optic coefficient of liquids

BY SIR VENKATA RAMAN, F.R.S., AND K. S. VENKATARAMAN

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1. INTRODUCTION

The variations in the refractive index of a liquid under external force may be expressed either in terms of the applied pressure or of the resulting change of density, in other words as proportional to the piezo-optic coefficient $(\partial\mu/\partial p)$ or to the elasto-optic coefficient $\rho(\partial\mu/\partial\rho)$. The ratio of the two coefficients is the compressibility β of the liquid; according as the pressure is applied adiabatically or isothermally, we have

$$\begin{aligned}(\partial\mu/\partial p)_\phi &= \rho(\partial\mu/\partial\rho)_\phi \cdot \beta_\phi && \text{(Entropy } \phi \text{ constant)} \\(\partial\mu/\partial p)_t &= \rho(\partial\mu/\partial\rho)_t \cdot \beta_t && \text{(Temperature } t \text{ constant).}\end{aligned}$$

In some important optical problems, e.g. the diffraction of light by ultrasonic waves, or the diffusion of light resulting from the Debye waves in a liquid, we are concerned with compressions and rarefactions occurring under adiabatic conditions and with the resulting changes of refractive index. As a rough approximation, the two elasto-optic coefficients may be taken to be equal and the two piezo-optic coefficients to be therefore in the ratio of the adiabatic and isothermal compressibilities. More exactly, however, these relations would not subsist, as a consequence of the refractive index of a dense fluid being in general a function of both density and temperature, and not of the density alone.

The piezo-optic coefficients under *isothermal* conditions for several liquids are known from the work of Röntgen and Zehnder (1891), Himstedt and Wertheimer (1922) and Eisele (1925), and the corresponding elasto-optic coefficients can be calculated from a knowledge of the isothermal compressibilities. No attempt appears, however, so far to have been made to determine the piezo-optic coefficient under *adiabatic* conditions directly by experiment. As the adiabatic coefficients and not the isothermal ones enter in some important applications of the subject, a knowledge of the former is clearly necessary. Further, as remarked above, the adiabatic and isothermal elasto-optic coefficients are not identical, and hence, the experimental determination of the adiabatic coefficient must be regarded as necessary even when

138 Sir Venkata Raman and K. S. Venkataraman

the isothermal coefficient is known with all desirable precision. It should be remarked in this connexion that the precise determination of the isothermal coefficient is not quite an easy matter. Any compression or expansion of the liquid necessarily produces a change of temperature, altering the refractive index, and unless the observations are made under conditions ensuring complete constancy of temperature, the determinations would not accurately give the effect of an isothermal compression. Experimentally, the situation is parallel to that arising in the determination of the compressibility of a liquid for small changes of pressure under isothermal conditions. As has been shown very clearly by Tyrer (1914), it is easier to make accurate determinations of the adiabatic compressibility than of the isothermal one. For the same reason, it should be easier with suitable technique to make precise determinations of the adiabatic piezo-optic coefficient and to calculate therefrom the adiabatic elasto-optic coefficient, than to measure and evaluate the corresponding isothermal coefficients.

Apart from the applications in ultra-sonic research and in the study of light scattering, precise determinations of the piezo-optic and elasto-optic coefficients for liquids have a special importance in relation to optical theory. It is well known that the Lorentz refraction formula does not accurately give the refractive index of a liquid in terms of the index for the vapour; the deviations from the formula are even more striking when we consider the changes in the refractive index of a liquid produced by changes of temperature or pressure. The explanation of these failures is a matter of considerable interest, and various attempts have been made (e.g. Raman and Krishnan 1928) to formulate theories giving better results. It is obvious that reliable experimental data regarding variations of refractive index under precisely defined physical conditions would be of value in testing such theories, and especially in determining the extent to which the refractivity of a dense fluid is a function of temperature independently of any changes in volume.

2. EXPERIMENTAL ARRANGEMENTS

In the work of Röntgen and Zehnder, as also of those who followed them, two parallel tubes of metal provided with optically worked end-windows of glass and immersed in a water-bath were employed to contain the liquid under study, and an interference method was employed to determine the changes in refraction. The optical paths through the two tubes were initially balanced against each other, and the interference fringes which moved past a fiduciary mark were counted one by one, as the pressure in one of the

Determination of adiabatic piezo-optic coefficient of liquids 139

tubes was slowly altered with reference to the pressure in the other. To enable the fringes to be kept in view without distortion and correctly counted, the rate of change of pressure had to be kept sufficiently small to allow temperature equalization to proceed simultaneously with the change of pressure; the final count was made after the fringes had settled down to a fixed position, indicating complete constancy of temperature. In the present investigation, on the other hand, the method has been employed of applying instantaneously to the liquid in one of the tubes, a pressure of the magnitude found necessary to make a known integral number of fringes shift past the reference mark, and then to release the pressure immediately afterwards, so that the observations could be repeated as often as desired without the fringes becoming distorted by irregular changes of temperature. Using tubes each 1 m. long, the pressure changes employed are of the order of 10 cm. of mercury or less, and the number of fringes that shift is also small (usually less than a dozen). As the observations are made under adiabatic conditions, the use of metal tubes and of a water-bath is not essential, and an interferential refractometer of the standard Rayleigh type with glass tubes has been successfully employed for the work.

The actual apparatus used in the work is the well-known laboratory interferometer made by the firm of Zeiss with the 1 m. glass tubes ordinarily provided for working with gases. In the instrument as employed, the upper half of a parallel beam of light proceeding from the collimator passes through a pair of apertures and then traverses the interferometer tubes containing the liquid under study, then through a pair of compensators and finally enters the observing telescope. The lower half of the beam from the collimator similarly passes below the interferometer tubes and through a single compensating plate into the observing telescope. Two sets of interference fringes are then seen, one below the other, through the eye-piece of the telescope, and these can be brought into coincidence by turning the drum attached to one of the compensators. On applying pressure to the liquid in one of the interferometer tubes, the upper system of fringes shifts, and if n be the number of fringes that shift on the application of a pressure p , measured in atmospheres, the change $d\mu$ in the refractive index is given by $ld\mu = n\lambda$, where l is the length of the tube, and λ is the wave-length of the light used. The change in refractive index for 1 atm. pressure will be

$$(\partial\mu/\partial p)_\phi = n\lambda \cdot 76/lp_0,$$

where p_0 is the pressure in cm. of mercury reduced to 0° C, sea-level and 45° latitude.

[*Added 5th April 1939.* It has been assumed above that the lengths of the two interferometer tubes remain identical in spite of the application of internal pressure in one of the tubes only. As the two tubes are rigidly attached to each other by hard wax along the whole of their length and the end-windows are fused on to both tubes jointly, any differential expansion is likely to be small. Its effect can obviously be completely eliminated if the two tubes are immersed in a bath of the same liquid as is contained in them. By a comparison of the values obtained for water with and without immersion in a water-bath, the differential expansion can be determined. This has been done and the small correction necessary thus evaluated. It has been found that on the introduction of the water-bath, there is a considerable improvement in the appearance and steadiness of the fringes and consequently also in the accuracy of measurement.]

The application of pressure to the liquid in one of the interferometer tubes is effected with the aid of a mercury manometer, one limb of which can be finely adjusted to any height above the other, by a winding drum and cog-wheel arrangement. The communication between the liquid in the interferometer and the mercury in the manometer is made through a tube containing water, the latter being prevented from mixing with the liquid under study by the attachment of a short U-shaped bend containing mercury to the interferometer tube. A large-bore three-way tap is interposed in the water column which transmits the pressure to the interferometer tube. The movable part of the manometer carries over the mercury a column of water of the height necessary to balance the weight of the connecting column of water on the other side. A cathetometer is used to read the levels of mercury in the manometer. After taking the initial reading and adjusting for the coincidence of one of the upper system of fringes with a reference fringe of the lower system by means of the interferometer drum, the manometer is cut off by turning the three-way tap, and its movable limb is raised to any convenient height. The pressure is then applied suddenly by opening the tap; there is then an instantaneous shift of the upper system of fringes. Generally, in the new position, no fringe coincides with the reference fringe. The pressure is then immediately released by turning the three-way tap so that the interferometer tube is connected to the atmosphere while the manometer is cut off. The movable limb of the manometer is raised or lowered as required and the experiment is repeated till an exact integral number of fringes shifts on the application of the pressure. The manometer being then cut off, the levels of mercury are read with the cathetometer. An auxiliary two-way tap between the manometer and the other tap serves to ensure that there is no leak from the manometer before the readings are

Determination of adiabatic piezo-optic coefficient of liquids 141

taken. A small correction for the change in the level of water in the fixed limb of the manometer on the application of pressure, has to be added to the difference in the levels of mercury. It is, of course, impossible to count the number of fringes that shift on the instantaneous application of pressure. But by a few trials with successively increasing pressures so that there is an increase of one fringe at a time in the shift, the exact number of fringes shifting at each pressure is easily ascertained.

The apparatus is set up in an underground cellar, where thermal disturbances are absent, and steady and straight fringes can therefore be observed in the interferometer. The latter is enclosed in a thick asbestos box and packed around with cotton, only two small openings being left for the passage of light. The interferometer tube, after being cleaned thoroughly, is completely filled with the liquid without leaving any air-bubble inside and is connected to the apparatus. The other end of the interferometer tube is tightly closed with a ground glass stopper which is then firmly fastened to it. The apparatus after being set up, is left undisturbed overnight to reach a constant temperature. A complete set of readings can then be taken in a few hours next morning. A Zeiss sodium lamp is used as the source of light, a large glass cell containing alum solution being placed in the path of the light to absorb the heat rays before they enter the interferometer. The temperature of the liquid is measured by a Centigrade thermometer reading up to 0.1° , inserted in the middle of the interferometer.

The liquids used were those supplied by Kahlbaum as purest and they were distilled again just before filling up the tube. The purity of the liquids was tested by determining their refractive indices with a Pulfrich refractometer and comparing them with the values taken from the standard tables. The agreement in every case was satisfactory.

3. RESULTS OF THE EXPERIMENTS

Half a dozen familiar liquids were chosen for the study and the method of observation was found to give satisfactory results in each case. Independent settings of the manometer pressure for a shift of a specified number of fringes in the interferometer agreed with themselves within less than 1%. Four or five such independent settings were made for each integral number of fringes shifting, and the mean of the same utilized for evaluating the piezo-optic coefficient. The results are recorded in Table I, and the final mean for each liquid is probably reliable to about 0.1% .

For the purpose of discussion, the final results for the liquids studied together with various other relevant physical constants taken from the

142 Sir Venkata Raman and K. S. Venkataraman

TABLE I. ADIABATIC PIEZO-OPTIC COEFFICIENTS

No. of fringes	Pressure reduced to 0° C, sea-level and 45° latitude $(\partial\mu/\partial p)_\phi \times 10^6$		No. of fringes	Pressure reduced to 0° C, sea-level and 45° latitude $(\partial\mu/\partial p)_\phi \times 10^6$	
Benzene at 24.0° C			Ethyl ether at 23.4° C		
3	3.726	36.06	3	2.624	51.19
4	4.979	35.97	4	3.482	51.44
5	6.212	36.04	5	4.348	51.50
6	7.437	36.13	6	5.216	51.52
7	8.682	36.11	7	6.074	51.60
			8	6.965	51.44
			9	7.823	51.51
	Mean	36.06 ± 0.03		Mean	51.46 ± 0.05
Carbon disulphide at 22.6° C			Methyl alcohol at 22.8° C		
4	4.048	44.25	3	3.939	34.10
5	5.072	44.15	4	5.189	34.52
6	6.064	44.31	5	6.545	34.22
7	7.086	44.24	6	7.834	34.30
8	8.137	44.02	7	9.107	34.43
9	9.133	44.13	8	10.368	34.56
10	10.143	44.16	9	11.689	34.46
11	11.091	44.43			
12	12.149	44.24			
	Mean	44.21 ± 0.04		Mean	34.37 ± 0.06
Chloroform at 23.2° C			Water at 23.1° C		
2	2.673	33.51	1	3.021	14.83
3	4.064	33.06	2	6.059	14.78
4	5.375	33.33	3	9.082	14.79
5	6.756	33.14	4	12.017	14.90
6	8.065	33.32			
7	9.410	33.32			
8	10.699	33.48			
	Mean	33.31 ± 0.06		Mean	14.83 ± 0.03

reference tables have been gathered together in Table II. The columns in this table, give respectively the liquid studied, its temperature, the refractive index as recorded and as observed by the authors, the coefficient of cubical expansion, the temperature coefficient of refractive index, the specific heat at constant pressure, the isothermal and adiabatic compressibilities and the isothermal and adiabatic piezo-optic coefficients.

[*Added 5th April 1939.* The values of the adiabatic piezo-optic coefficients have been corrected for the differential expansion of the tubes mentioned above. The correction amounts to 1.16% for water and varies between 0.35% and 0.88% for other liquids.]

Determination of adiabatic piezo-optic coefficient of liquids 143

TABLE II. DATA FOR LIQUIDS STUDIED

Liquid	Temp. ° C	μ (<i>I.C.T.</i>)	μ (authors)	$\alpha \times 10^5$	$(\partial\mu/\partial t)_p$ $\times 10^5$	C_p	$\beta_t \times 10^6$	$\beta_\phi \times 10^6$	$(\partial\mu/\partial p)_t$ $\times 10^6$	$(\partial\mu/\partial p)_\phi$ $\times 10^6$
Benzene	24.0	1.4988	1.4988	122.3	-65.0	0.4076	98.7	68.6	51.94	35.80
Carbon di- sulphide	22.6	1.6258	1.6261	119.8	-80.5	0.2389	95.6	61.6	66.81	43.89
Chloroform	23.2	1.4434	1.4430	127.7	-58.8	0.2333	104.0	70.2	—	33.02
Chloroform	15.0	—	—	125.3	—	—	97.0	65.6	47.31	—
Ethyl ether	23.4	1.3506	1.3506	165.1	-58.6	0.5431	196.7	146.9	71.22	51.28
Methyl alcohol	22.8	1.3280	1.3281	119.7	-36.0	0.612	125.0	104.0	42.25	34.21
Water	23.1	1.3327	1.3326	23.84	-9.65	1.000	46.06	45.6	14.98	14.66

SOURCES OF DATA. *International Critical Tables (I.C.T.)* and Landolt-Bornstein Tabellen (*L.B.T.*). For the coefficient of cubical expansion, $\alpha \times 10^5$: for all liquids except water—*I.C.T.* density-temperature relations. The values agree well with the available experimental data. For water—*I.C.T.* from the volume of 1 g. of water at different temperatures.

For the temperature coefficient of refractive index $(\partial\mu/\partial t)_p \times 10^5$ —from *L.B.T.* and *I.C.T.* as nearly as possible at the temperatures required.

For the specific heat at constant volume, C_p : for water and ethyl ether from *I.C.T.* and for other liquids, mean of the available values given in Shiba (1931).

For the isothermal compressibility, $\beta_t \times 10^6$: the values were calculated thermodynamically from β_ϕ (Tyrer 1914). They agree fairly well with the values determined experimentally, but are more reliable than the latter. The experimental data tend to be slightly too small, owing to the compression not being quite isothermal.

For the adiabatic compressibility, $\beta_\phi \times 10^6$ —Tyrer (1914).

For the isothermal piezo-optic coefficient $(\partial\mu/\partial p)_t \times 10^6$: for chloroform—Himstedt and Wertheimer (1922); for all other liquids—Röntgen and Zehnder (1891).

4. DISCUSSION OF RESULTS

(a) *Deviations from the Lorentz refraction formula.* Differentiating the Lorentz formula, we find

$$\rho(d\mu/d\rho)_{\text{Lor}} = (\mu^2 - 1)(\mu^2 + 2)/6\mu.$$

The formula presupposes that the refractive index is a function of the density alone; in other words, it is assumed that $\rho(d\mu/d\rho)$ should be the same in all cases, e.g. for a change in density due to alteration of temperature under constant pressure, or due to alteration of pressure under constant entropy or at constant temperature. We should thus find that

$$-\frac{1}{\alpha} \left(\frac{\partial\mu}{\partial t} \right)_p = \frac{1}{\beta_\phi} \left(\frac{\partial\mu}{\partial p} \right)_\phi = \frac{1}{\beta_t} \left(\frac{\partial\mu}{\partial p} \right)_t = \frac{(\mu^2 - 1)(\mu^2 + 2)}{6\mu}.$$

144 Sir Venkata Raman and K. S. Venkataraman

How far these relations are in agreement with reality will be evident on a comparison of the last four columns of Table III in which the quantities concerned have been tabulated. It is seen that the variation of refractive index indicated by the Lorentz formula is invariably larger than that actually observed for pressure changes, while there are similar large differences, between the theoretical and observed values for temperature changes which except in the case of water are in the same general direction. Comparing the values amongst themselves, it is noteworthy that in the case of benzene, which is a typical non-associated liquid, the variations of refractive index for equivalent pressure and temperature changes differ very little, while for methyl alcohol and water, which are strongly associated liquids, they differ notably, though remarkably enough, in opposite directions for these two liquids. Chloroform and ether which are polar but not highly associated liquids, show less striking differences. The deviations from the Lorentz formula are very pronounced for carbon disulphide which has the highest refractive index as well as the highest degree of optical anisotropy for its molecules amongst the six liquids studied.

TABLE III. DEVIATIONS FROM LORENTZ REFRACTION FORMULA

Liquid	Temp. ° C	$-\frac{1}{\alpha} \left(\frac{\partial \mu}{\partial t} \right)_p$	$\frac{1}{\beta_t} \left(\frac{\partial \mu}{\partial p} \right)_t$	$\frac{1}{\beta_\phi} \left(\frac{\partial \mu}{\partial p} \right)_\phi$	$\frac{(\mu^2 - 1)(\mu^2 + 2)}{6\mu}$
Benzene	24.0	0.5315	0.5262	0.5219	0.5887
Carbon disulphide	22.6	0.6719	0.6988	0.7125	0.7818
Chloroform	23.2	0.4605	0.4877	0.4704	0.5106
			(at 15° C)		
Ethyl ether	23.4	0.3549	0.3620	0.3490	0.3889
Methyl alcohol	22.8	0.3007	0.3380	0.3290	0.3609
Water	23.1	0.4048	0.3253	0.3215	0.3664

(b) *Temperature variation of refraction at constant density.* The coefficient of temperature variation of refractive index $(\partial \mu / \partial t)_\rho$ at constant density can be calculated by comparing the change of refractive index with rise of temperature at constant pressure with that produced by compression, isothermal or adiabatic, as the case may be. The necessary formulae which are very readily derived are

$$(\partial \mu / \partial t)_\rho = \{ \alpha (\partial \mu / \partial p)_t + \beta_t (\partial \mu / \partial t)_p \} / \beta_t,$$

and
$$(\partial \mu / \partial t)_\rho = \{ \alpha (\partial \mu / \partial p)_\phi + \beta_\phi (\partial \mu / \partial t)_p \} / \{ \alpha (\partial t / \partial p)_\phi + \beta_\phi \}.$$

The first formula involves the piezo-optic coefficient at constant temperature and the second the piezo-optic coefficient at constant entropy. Table IV

Determination of adiabatic piezo-optic coefficient of liquids 145

shows in its third and fourth columns the results calculated respectively from these two formulae. It will be seen that these are in fair agreement, except in the case of chloroform and of ether where the isothermal data are probably not reliable. The figures leave little doubt as to the reality of the variation of the refractive index of a liquid with temperature at constant density. The magnitude of this variation, in relation to the ordinary temperature coefficient of the refractive index at constant pressure (shown in the fifth column for comparison) is largest in the case of the highly associated liquids, water and methyl alcohol, but has the opposite sign in these two liquids. It is small but quite definite and has the same sign for benzene as the ordinary temperature coefficient, while in carbon disulphide, it is both relatively and absolutely much larger than for benzene but of the opposite sign. The significance of these results awaits fuller elucidation.

TABLE IV. VARIATION OF REFRACTION WITH TEMPERATURE
AT CONSTANT VOLUME

Liquid	Temp. ° C	$(\partial\mu/\partial t)_\rho \times 10^5$	$(\partial\mu/\partial t)_\rho \times 10^5$	$(\partial\mu/\partial t)_p \times 10^5$
		calculated from isothermal coefficients	calculated from adiabatic coefficients	
Benzene	24.0	-0.64	-0.85	-65.0
Carbon disulphide	22.6	+3.23	+2.86	-80.5
Chloroform	23.2	+2.30	+0.74	-58.8
		(at 15° C)		
Ethyl ether	23.4	+1.17	-0.78	-58.6
Methyl alcohol	22.8	+4.5	+2.91	-36.0
Water	23.1	-1.90	-1.97	-9.65

(c) *Relation between adiabatic and isothermal piezo-optic coefficients.* Owing to the existence of a pure temperature effect on refractive index evaluated and shown in Table IV, the ratio of the adiabatic and the isothermal piezo-optic coefficients is not exactly the same as the ratio of the corresponding compressibilities. The correction necessary appears as the second term in the following formula:

$$(\partial\mu/\partial p)_\phi = (\partial\mu/\partial p)_t \beta_\phi / \beta_t + (\partial\mu/\partial t)_\rho (\partial t/\partial p)_\phi.$$

The first term on the right-hand side is the approximate value of the adiabatic coefficient in terms of the isothermal one, while the second term which is the correction can be evaluated from the values of $(\partial\mu/\partial t)_\rho$ shown in the fourth column of Table IV.

146 Sir Venkata Raman and K. S. Venkataraman

Table V shows the quantities involved. It is seen that in all cases except methyl alcohol, the correction term improves the agreement between the observed and calculated values of $(\partial\mu/\partial p)_\phi$, though evidently the accuracy of determination of the isothermal coefficients on which the calculations are based is insufficient to make such improvement at all impressive.

TABLE V. RELATION OF ADIABATIC TO ISOTHERMAL
PIEZO-OPTIC COEFFICIENTS

Liquid	Temp. ° C	$\left(\frac{\partial\mu}{\partial t}\right)_\rho \left(\frac{\partial t}{\partial p}\right)_\phi \times 10^6$	$\left(\frac{\partial\mu}{\partial p}\right)_t \frac{\beta_\phi}{\beta_t} \times 10^6$	$(\partial\mu/\partial p)_\phi \times 10^6$ (calculated) sum of cols. 3 and 4	$(\partial\mu/\partial p)_\phi \times 10^6$ (observed)
Benzene	24.0	-0.18	36.10	35.92	35.80
Carbon disulphide	22.6	+1.03	43.05	44.08	43.89
Chloroform	23.2	+0.29	32.00	32.29	33.02
			(at 15° C)		
Ethyl ether	23.4	-0.17	53.19	53.02	51.28
Methyl alcohol	22.8	+0.41	35.15	35.56	34.21
Water	23.1	-0.03	14.84	14.81	14.66

SUMMARY

The piezo-optic coefficient defining the change of refractive index of liquids with pressure has till now been measured only for the case of isothermal compression. In such important applications, however, as the theory of the diffraction of light in ultra-sonic fields and of the scattering of light in liquids by the Debye waves, it is the effect of adiabatically applied pressure on the refractive index which requires to be known. In the present paper, an experimental technique is described which enables the adiabatic piezo-optic coefficients of liquids to be measured with standard laboratory equipment and actually with greater ease and precision than the corresponding isothermal coefficient. The resulting data for six common liquids are discussed with reference to (1) the deviations from the Lorentz refraction formula, (2) the variation of refractive index with change of temperature when the density is maintained constant, (3) the relation between the adiabatic and isothermal piezo-optic coefficients. These three matters are shown to be closely connected. The data and the discussion based thereupon show clearly that the present technique opens up a field of research which is of considerable interest in relation to the optical properties of liquids and their molecular structure.

Determination of adiabatic piezo-optic coefficient of liquids 147

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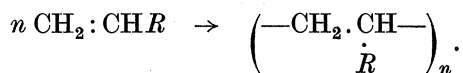
The mechanism of polymerization reactions

I. The polymerization of styrene and
methyl methacrylate

BY R. G. W. NORRISH, F.R.S. AND E. F. BROOKMAN

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In the polymerization of styrene, methyl methacrylate, the acrylates including acrylic acid, vinyl acetate, methylvinyl-ketone, vinyl halides, indene and coumarone, the monovinyl compound of the formula $\text{CH}_2 : \text{CH} \cdot R$ is capable of growing into long saturated molecules through the reaction of the olefinic link:



The type of polymerization which is manifested by all these compounds is of a very simple character because only one reactant is involved and one, moreover, whose functionality is limited to two. This means that only straight chains can be produced, and with the simple monovinyl compounds no cross-linking is possible.

It has been established that the rate of polymerization depends upon two important factors: (a) the presence of catalyst, and (b) the temperature of reaction. Even in the case of the "pure" substances it is probable that reaction is dependent upon traces of catalyst. At least in one case, that of vinyl acetate (Cuthbertson, Gee and Rideal 1937), it has been shown that complete exclusion of active catalyst confers a high degree of stability on the monomeric substance. The nature of catalysts is varied, but perhaps the