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Studies on the Decomposition of Azomethane

III. Effect of Various Inert Gases¹

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Data are presented on the decomposition of azomethane in the presence of several inert gases, relative activation efficiencies being given in Table II. The low efficiency of helium as compared to the other gases is taken as indicating that exchange of vibrational energy between molecules is more probable than the transition of translational into vibrational energy. The results are compared with other pertinent data, and the probable mechanism of energy exchange is discussed. Finally, some preliminary data on the effect of azomethane on reactive gases are given.

IN Part II³ of this series of papers we presented data on the decomposition of azomethane in the presence of helium and calculated the relative activating efficiency of helium as compared to azomethane itself. In this paper we shall present and discuss data showing the effects of various other inert gases.

§1. EXPERIMENTAL DETAILS

The apparatus used was that described in Part I,⁴ and the manipulations and general technique were the same as previously used. The various materials used were prepared as follows:

Deuterium, stated to be better than 99.5 percent pure, was kindly furnished by Professor Taylor of the Princeton Laboratory.

Nitrogen was taken from a tank, passed over hot copper, hot copper oxide, through alkaline pyrogallol, through a trap cooled in dry ice, and over fused potassium hydroxide.

Methane was prepared by the hydrolysis of methyl magnesium iodide in dibutyl ether solution, passed through two traps cooled by dry ice, bubbled through more methyl magnesium iodide in dibutyl ether solution, passed through another dry ice trap, condensed in a liquid air trap, pumped off, and distilled, the middle fraction being used.

Carbon monoxide was made by dropping 85 percent C.P. formic acid into concentrated sulfuric acid (both having been pumped off beforehand to remove other gases). It was then passed through two traps cooled by dry ice, through a wash bottle of alkaline pyrogallol, and through a third dry ice trap. About eight liters were run through the train before the sample used was collected.

Carbon dioxide was made by heating an evacuated vessel containing pure sodium bicarbonate. The gas was passed through two dry ice traps, condensed by means of liquid air, and distilled from dry ice to liquid air.

Mixtures of azomethane (prepared as in Part II) with the various inert gases were made in one of two ways. In the first method the azomethane was admitted to the storage bulb at a known pressure, condensed in a liquid air trap, the inert gas admitted and its pressure measured, and the azomethane then allowed to evaporate into the bulb. Such a mixture was allowed to stand overnight before using. In the second method the inert gas was admitted without condensing the azomethane and the total pressure measured. Such a mixture, having been well stirred in the process of making it, was sometimes used after a lapse of two hours. This would perhaps not allow sufficient time for complete mixing throughout all the connecting tubing, but the volume of the latter was negligibly small.

Generally when the gas was admitted from the storage bulb into the reaction vessel, equilibrium between them (requiring only 15–20 seconds) was allowed to become established and the initial pressure taken as the remaining pressure in the storage flask. In the case of a few runs made with water vapor as an inert gas, it being impractical to use large pressures, it was considered more accurate to calculate the initial pressures in the second and third runs made from the measured pressure for the first run and the known pressure distribution ratio between the reaction vessel and the storage flask. This pressure ratio served as a check on the initial pressure in the other cases. A few bad runs are connected with an error in the initial pressure reading, but as the source of this error was not known these runs are presented with the others, though they are not generally used in making up averages.

Mr. A. K. Solomon informs us that he has observed slow decomposition of azomethane in diffuse light, but we found no systematic changes in our results from allowing a mixture to stand in the storage bulb for a day, and we believe errors due to this cause are negligible.

§2. THE EXPERIMENTAL RESULTS

The initial rate of decomposition of azomethane in the inert gas mixtures was calculated from the rate of pressure increase and corrected for the external volume as in Part II. The relative activating efficiency, α , of the inert gas compared

¹ Presented at the San Francisco meeting of the American Chemical Society, August, 1935.

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³ J. Chem. Phys. 4, 242 (1936).

⁴ J. Chem. Phys. 4, 239 (1936).

to azomethane at the same pressure was also obtained as before, using the curves of Fig. 1 of Part II to obtain the rate of decomposition of pure azomethane. The results are given in Table I, and some of them are also presented graphically in Figs. 1 and 2. In Table II we summarize the average values of α , including that for helium, and we also give the values, α' , of the relative activating efficiency *per collision*, referred to azomethane as unity. From the formulas for the number of collisions between activated azomethane molecules and other molecules it may readily be seen that

$$\alpha' = \alpha [2M/(M + M_0)]^{1/2} [2\sigma_0/(\sigma + \sigma_0)]^2, \quad (1)$$

where M and M_0 are the molecular weights of the

TABLE I. Summary of results. (P_i =initial azomethane pressure in mm, P_{D_2} =deuterium pressure, etc.; K =initial rate constant in sec.⁻¹.)

Run	Log P_i	Log ($K \times 10^3$)	α	Run	Log P_i	Log ($K \times 10^3$)	α
$P_{D_2}/P_i = 5.00; 310^\circ\text{C}$				$P_{CH_4}/P_i = 4.98, \text{ cont.}$			
126	0.929	1.755	0.67	189	0.043	1.359	0.25
127	.607	1.671	.71	190	1.727	1.205	.20
128	.291	1.550	.62	191	1.415	1.165	.49
129	.069	1.107					
130	1.718	1.339	.65				
$P_{D_2}/P_i = 9.95; 310^\circ\text{C}$				$P_{CH_4}/P_i = 10.01; 310^\circ\text{C}$			
				192	0.691	1.662	0.25
141	0.710	1.808	1.06	193	.372	1.547	.23
142	.393	1.700	0.83	194	.055	1.435	.24
143	.076	1.582	.74	195	1.736	1.306	.24
144	1.757	1.438	.59	196	1.420	1.163	.24
$P_{D_2}/P_i = 6.00; 290.4^\circ\text{C}$				$P_{CO}/P_i = 5.01; 310^\circ\text{C}$			
145	0.925	1.135	0.51	250	0.984	1.628	0.08
146	.600	1.081	.75	251	.664	1.537	.12
147	.277	0.974	.65	252	.343	1.428	.13
148	1.955	.873	.70	253	.025	1.292	.13
149	1.633	.658	.35	254	1.713	1.128	.09
$P_{D_2}/P_i = 3.02; 290.4^\circ\text{C}$				$P_{CO}/P_i = 10.00; 310^\circ\text{C}$			
150	0.858	1.105	0.88	255	0.735	1.625	0.14
151	.537	0.953	.45	256	.413	1.497	.12
153	1.891	.712	.44	257	.095	1.389	.13
				258	1.777	1.257	.14
$P_{N_2}/P_i = 5.04; 310^\circ\text{C}$				$P_{CO_2}/P_i = 5.03; 310^\circ\text{C}$			
171	0.977	1.671	0.19	301	0.992	1.667	0.16
172	.659	1.568	.20	302	.670	1.574	.20
173	.342	1.455	.19	303	.347	1.461	.20
174	.093	1.234		304	.029	1.350	.24
175	1.761	1.043		305	1.711	1.199	.21
				306	1.400	1.055	.23
$P_{N_2}/P_i = 5.05; 310^\circ\text{C}$				$P_{CO_2}/P_i = 9.95; 310^\circ\text{C}$			
176	0.973	1.705	0.30	307	0.718	1.626	0.16
177	.656	1.580	.23	308	.396	1.541	.20
179	.028	1.348	.23	309	.077	1.433	.22
180	1.714	1.154	.13	310	1.759	1.304	.22
				311	1.442	1.151	.20
$P_{N_2}/P_i = 9.99; 310^\circ\text{C}$				$P_{CO_2}/P_i = 50.0; 310^\circ\text{C}$			
181	0.748	1.663	0.21	312	0.066	1.600	0.17
182	.430	1.538	.18	313	1.746	1.507	.20
183	.113	1.418	.17	314	1.426	1.376	.18
184	1.797	1.261	.13				
185	1.484	1.105	.12				
$P_{CH_4}/P_i = 4.98; 310^\circ\text{C}$				$P_{H_2O}/P_i = 0.98; 310^\circ\text{C}$			
186	0.995	1.678	0.19	315	0.704	1.528	0.38
187	.676	1.590	.24	316	.387	1.418	.44
188	.357	1.485	.26	317	.068	1.282	.41

TABLE II. Relative activation efficiencies.

Substance	σ	α	α'
Azomethane	1.76	1.00	1.00
N ₂	1.23	0.19	0.21
CO	1.24	.12	.13
CH ₄	1.33	.23	.20
H ₂ O	1.00	.41	.46
CO ₂	1.28	.20	.25
D ₂	1.07	.66	.37
He	1.00	.12	.07

inert gas and azomethane, respectively, and σ and σ_0 are their respective kinetic theory radii (relative values only). Most of these values were taken from Binkele;⁵ the value for azomethane was assumed to be the same as that of propane.⁶ For deuterium the value for hydrogen was used. The values used are given in Table II.

A few experiments on the effect of nitrogen on the azomethane decomposition have been made by Ramsperger.⁷ His value of α is in good agreement with ours, though the significance of this may be doubted in view of the difference between his results and ours on pure azomethane.

Table I contains all runs made with the inert gases listed except one with deuterium (No. 152) in which there was a marked variation in rate during the run and one with nitrogen (No. 178) which was known to be spoiled. In a few cases in which some gross error must have been made α was not calculated, nor were the results included in Fig. 1 or 2. No. 191. was not included in calculating the average for methane. The run numbers may be correlated with those given in Part II. Runs not appearing in either paper represent runs made in the presence of gases which were not inert (see §4, below).

§3. DISCUSSION OF THE RESULTS

In all cases considered here the values of α for any given gas are the same within the experimental error over the range of conditions studied. The most erratic results occurred with deuterium, but even in this case Fig. 1 indicates that while there is some scattering of the points there appears to be no appreciable trend away from that predicted for an inert gas. This is, indeed, rather remarkable in this particular case, for we found, in a series of experiments which will be reported later, that the apparent value of α shows marked trends with pressure and

⁵ Binkele, Ann. d. Physik **15**, 729 (1932).

⁶ Melaven and Mack, J. Am. Chem. Soc. **54**, 899 (1932).

⁷ Ramsperger, J. Phys. Chem. **34**, 669 (1930).

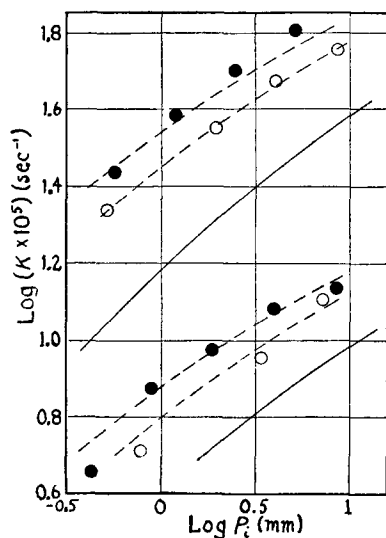


FIG. 1. Effect of deuterium. The solid curves are for pure azomethane at 310°C and 290.4°C. The broken curves are for deuterium mixtures, of the compositions given in Table I, assuming $\alpha=0.66$. At each temperature the black circles go up with the upper broken curve, the open circles go with the lower broken curve.

especially with the composition of the mixture in the case of hydrogen (α increases with increasing percent of hydrogen). This is probably due, at least in part, to reaction of the methyl radicals, formed in the decomposition of the azomethane, with H_2 , forming methane and releasing a hydrogen atom, which then reacts further, possibly with the azomethane. The amount of reaction is not so great but that an uncritical examination might lead one to believe that hydrogen is simply activating the azomethane; on the other hand it is sufficiently marked so that one would expect to observe variations of α also, if to a somewhat smaller extent, in the case of deuterium. We can only conclude from our results that either the methyl radical reacts much more slowly with deuterium, or else that the deuterium atom is less active than the hydrogen atom, and that this difference is great enough so that deuterium may be considered to be practically an inert gas. Tentatively, at least, we believe that the value of α obtained may be taken as giving the true indication of the relative activating efficiency of deuterium.

We have pointed out in our previous work that the constancy of α for helium over a range of conditions furnishes evidence that the azo-

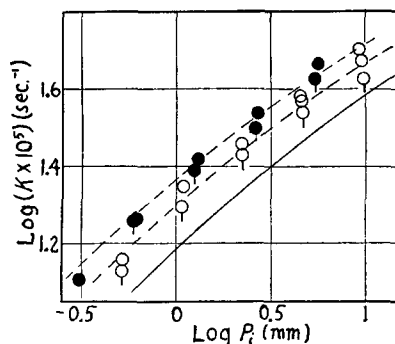


FIG. 2. Effect of nitrogen and of carbon monoxide. Solid line, pure azomethane, 310°C. Broken lines 5 : 1 and 10 : 1 mixtures with $\alpha=0.16$. Black circles, 10 : 1 mixtures. Open circles, 5 : 1 mixtures. Circles without tail, N_2 . Circles with tail, CO.

methane decomposition is not a chain reaction, or at least that the chain length is independent of the pressure over the range of pressures studied. The results obtained in this paper reinforce this view. Particularly noteworthy in this connection are the data with carbon dioxide, in which the constancy of α is maintained not only over the usual pressure range but over a very considerable range in the composition of the mixtures used.

Let us now turn our attention to a consideration of the variation of α' for the different gases studied. Most striking is the difference between deuterium and helium and in particular the low efficiency of helium. On account of the almost complete spherical symmetry of the electron distribution in the outermost ranges of the deuterium molecule, it hardly seems possible that as great a difference as exists between these two gases can be due to the possibility of exchange of rotational energy by the deuterium. Though this can hardly be said to be proved, it suggests that a large part of the difference between helium and the other molecules in general is to be ascribed to the exchange of vibrational energy between molecules being a more probable process than a change from translational into vibrational energy, or *vice versa*.⁸ The relatively

⁸ It is of course still necessary, in general, for some transfer of energy between translational and vibrational types to take place, but the amount will be much less, and the theory (reference 11) indicates that it is easier for a small amount of energy to be so transferred than a large amount.

Added in proof: Since submitting this paper we have seen the article of Patat and Bartholomé, *Zeits. f. physik.*

small efficiency of helium finds a counterpart in the work of Koblitz and Schumacher⁹ on the F_2O decomposition, but Volmer⁴ and his co-workers¹⁰ found that helium was a better activator than nitrogen or oxygen in the N_2O decomposition.

Some theoretical calculations on the exchange of translational and vibrational energy have been published by one of us.¹¹ The approximations it was necessary to make limit the range of applicability of these calculations, so that they probably cannot be counted upon to give information in cases in which the colliding body is heavier than helium. They brought out, however, the various factors upon which such probabilities depend—the mass of the colliding particle, the “sharpness” of the collision, the amount of energy transferred from translation to vibration, the nature of the vibrators, etc. These factors and others will enter in a still more complicated way when there is exchange of vibrational energy between oscillators, and the obvious difficulty in interpreting the results of various experimenters cited at the end of the preceding paragraph makes it seem futile to attempt a theoretical discussion of the values of α' at the present time. It may, however, be of interest to note that the compounds containing light atoms, which we may infer would tend to participate in “sharp” collisions, have the largest values of α' in our experiments, except for the very symmetrical methane. The low bending frequency of carbon dioxide does not seem to result in its having a large value of α' , as might, off-hand, have been expected.

Perhaps the most remarkable feature about the results of the present paper, as well as those of Koblitz and Schumacher and Volmer and his coworkers, and also those of Schumacher and Sprenger¹² who studied the decomposition of NO_2Cl , is the small range of the values of α' . In particular we should like to call attention to the relatively small difference between nitrogen

and carbon monoxide; as will be indicated by an inspection of Fig. 2 the difference between them is practically within the limits of experimental error. This is in marked contrast to results on the transfer of energy between carbon monoxide or nitrogen and chlorine,¹³ and between carbon monoxide or nitrogen and oxygen¹⁴ obtained from acoustical experiments. It must of course be noted that the processes occurring in acoustical experiments are rather different from those occurring in reaction rate experiments. The dispersion of sound depends upon the rapidity with which equilibrium is established between translational and vibrational degrees of freedom and hence measures the rate of transfer between vibrational and translational energy rather than between two types of vibrational energy. Furthermore simpler molecules have been studied acoustically and activated molecules are not involved. Nevertheless it is difficult to understand why reaction rate experiments and acoustical experiments give such different results. The writers of the acoustical papers have invoked two different hypotheses to explain their observations. The difference between the effects of carbon monoxide and nitrogen on oxygen has been ascribed to the electric moment of the former,¹⁴ and the difference between their action on chlorine has been related to the fact that carbon monoxide and chlorine can be thought of as combining to form phosgene.¹³ Whether these hypotheses can be considered reasonable on *a priori* grounds will depend upon whether the forces due to the dipole moment of carbon monoxide on the one hand, or the chemical forces between it and chlorine on the other, are comparable to the ordinary van der Waals and repulsive forces in the average collision at which energy is exchanged. In our opinion it is very unlikely that this is the case. If the dipole moment of carbon monoxide were of importance we should not expect the physical properties to be so similar to those of nitrogen. And it is well known that the chemical forces have in general a smaller range of action than the van der Waals and repulsive forces. When two chemically saturated molecules collide the first forces to

Chemie **B32**, 396 (1936), which is of interest in this connection.

⁹ Koblitz and Schumacher, Zeits. f. physik. Chemie **B25**, 283 (1934).

¹⁰ See Volmer and Bogdan, Zeits. f. physik. Chemie **B21**, 271 (1933).

¹¹ O. K. Rice, J. Am. Chem. Soc. **54**, 4558 (1932). See also Zener, Phys. Rev. **37**, 556 (1931).

¹² Schumacher and Sprenger, Zeits. f. physik. Chemie **B12**, 115 (1931).

¹³ Eucken and Becker, Zeits. f. physik. Chemie **B27**, 261 (1934). See also Franck and Eucken, *ibid.* **B20**, 460 (1933).

¹⁴ Kneser and Knudsen, Ann. d. Physik **21**, 682 (1934).

come into play are the van der Waals forces; at smaller distances the repulsive forces start to operate; at still smaller distance forces of the Heitler-London exchange type *may* become important, but the relative energy of the molecules must be large in order for them to get close enough for this to happen. It is true that the acoustical experiments indicate a slight positive temperature coefficient for the exchange of energy, so that it seems that molecules with excess relative energy exchange energy more readily, but the indicated activation energies are not very large and it seems unlikely to us that chemical forces can play a great role. If these considerations are correct, the transfer of energy may be thought of as taking place between two collections of atoms, the atoms in each group being tightly held together, and the interaction of the atoms of one group with those of the other being like an interaction between billiard balls—not hard billiard balls, to be sure, but “squashy” ones, this being essentially the assumption of Rice and Zener.¹⁵ For an interaction of this sort carbon monoxide ought to resemble nitrogen, which accords fairly well with our results, but leaves the acoustical work unexplained.

Finally, we must make note of the great difference in the absolute values of the efficiency of energy transfer in the acoustical and the kinetic experiments. In the former the collision efficiency ranges from around 3×10^{-2} to about 10^{-6} , but most of the values are in the lower ranges. In the case of F_2O Koblitz and Schumacher have shown that the absolute collision efficiency is of the order of 1. Volmer has concluded in the case of N_2O that perhaps only one collision in 200 of an activated molecule leads to deactivation. However, if not all the degrees of freedom of N_2O , but rather only one, is involved in the reaction, then the calculated number of activated molecules becomes smaller and it would be possible to assume an efficiency¹⁵ of 1 for deactivation of N_2O by N_2O . Since N_2O is a linear molecule it seems quite likely that there is no transfer of energy between stretching and bending vibra-

tions. Furthermore, the decomposition of N_2O presumably does not involve the breaking of a bond, but rather a predissociation. This predissociation is probably very definitely associated with one particular normal (or approximately normal) vibration, in contrast to the breaking of a bond. It has previously been suggested that only one vibration is concerned (at least at high pressures) in the case of the decomposition of NO_2Cl , which also probably involves a predissociation.¹⁶ In the case of the azomethane decomposition, on account of the great number of degrees of freedom involved, the range of their frequencies, and the fact that the bimolecular stage of the reaction is never reached experimentally, it is not practical to attempt to make a very accurate estimate of the number of activated molecules, and hence it is not possible to say just what the deactivational efficiency is, but there is no evidence against its being of the order of 1, and this would make the efficiency of helium fairly close to what might be expected from the calculations of Rice.

§4. PRELIMINARY NOTICE OF EXPERIMENTS WITH REACTING GASES

We should like to note here some results obtained with gases which apparently are not inert. We have already observed that in the case of hydrogen α does not appear to be constant. A similar result was found with ethane as the “inert” gas, but in this case α seemed to depend most strongly on the pressure in a given mixture, increasing as the pressure decreased. Our values were not only not constant, but in all cases were lower than those found by Ramsperger.⁷ It is possible that Ramsperger's ethane contained some diethyl ether, as he used this as a solvent in preparing his ethane, while we used the higher boiling dibutyl ether. We obtained results with propane which were very similar in every detail to those obtained with ethane. But, in marked contrast, azomethane starts a chain decomposition in isobutane.

The inconstancy of α in the cases of ethane and propane is presumably due to the occurrence of side reactions. These side reactions probably

¹⁵ Ramsperger and Waddington, Proc. Nat. Acad. Sci. **17**, 103 (1931); Hunter, Proc. Roy. Soc. **A144**, 386 (1934), however, does not agree with Volmer and his collaborators on the activation energy for this reaction. In view of this fact and the correction which a change of the activation energy would entail, the case of N_2O may be in some doubt.

¹⁶ O. K. Rice and Sickman, J. Am. Chem. Soc. **56**, 1450 (1934).

result from the presence of methyl radicals which can remove a hydrogen atom from many organic molecules, forming methane and a more complicated free radical which may then react further. The great difference in the effect of methyl radicals on various organic substances, some of them quite similar, is of considerable interest. Azomethane itself is presumably very little attacked if at all. It is impossible to say whether methane reacts with methyls or not as the products would be the same as the reactants. Ethane and propane are presumably only slightly attacked by methyls, but isobutane, acetaldehyde¹⁷ and propionaldehyde¹⁸ are so readily attacked at the temperature at which azomethane decomposes that the side reaction becomes a main reaction. It is, of course, to be remarked that relatively small differences in the activation energies involved would account for the observed effects.

¹⁷ Allen and Sickman, J. Am. Chem. Soc. **56**, 2031 (1934).

¹⁸ O. K. Rice and Sickman, J. Am. Chem. Soc. **57**, 1384 (1935).

The kinetics of the polymerization of ethylene induced by methyl radicals from azomethane has already been described in outline.¹⁸ It should be remarked that it is the over-all rate of change of pressure with time which is proportional to the square root of the azomethane pressure and the three-halves power of the ethylene pressure. When an attempt is made to correct for the increase of pressure produced by the decomposition of azomethane this simple relation seems to be upset.

Azomethane also causes propylene to polymerize. The reaction is, we believe, similar to the ethylene polymerization. Acetylene also polymerizes under the influence of methyl radicals from azomethane, the rate of pressure change being proportional to the square root of the azomethane pressure and to the first power of the acetylene pressure, a rather more usual result. These various reactions will be described in detail later.

Erratum. In Part II an error was made in the calculations for Run 217. For this run $\log P_i$ should be 0.295 and $\log (K \times 10^5)$ should be 0.691.

The Effect of Structure Upon the Reactions of Organic Compounds. Temperature and Solvent Influences

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(Received June 1, 1936)

The effect of a substituent upon the heat of ionization of an organic acid is far from identical with its effect upon the free energy of ionization. In the case of benzoic acid derivatives the entropy of ionization varies with structure in a way which can be predicted from the temperature dependence of the dielectric constant of the solvent, and which is closely correlated with the effect of a change in the dielectric constant of the solvent upon the relative strengths of substituted and unsubstituted acids. The behavior of aliphatic acids is more complicated, probably because of their less rigid structure. Similar considerations apply to the effect of changes in structure of reactant upon other equilibria and upon reaction rates.

THE effect of a change in structure of reactant upon the equilibrium or rate of an organic chemical reaction has been interpreted in a variety of ways.¹ Thus the shift in the ionization constant of formic acid produced by the substiti-

tution of another group for the nonionizable hydrogen has been attributed to an increase or decrease in the electrical work involved in separating the ions of the acid which results either from the dipole field of the substituent or from internal electron displacements of various sorts produced by the substitution. These interpretations have in common an identification

¹ See for instance: Waters, *Physical Aspects of Organic Chemistry* (New York, 1936); or Ingold, *Chem. Rev.* **15**, 225 (1934).