

at the several maxima are as follows: 23.4° for the 64° isotherm; 21.9° for the 69° isotherm; 19.7° for the 75° isotherm; 18.4° for the 80° isotherm.

The 15°C. isotherm rises with a slight upward inflection with an average Joule-Thomson coefficient of approximately two degrees warming per 68 atm. of pressure drop.

Comparisons are made with Joule-Thomson effects computed from hydrogen data of state and other appropriate data.

A table of heat contents, as a function of pressure and of temperature, is computed from the smooth isotherms of our data.

Curves are also given for the thermodynamic efficiency of hydrogen liquefaction as functions of temperature and pressures, computed from our measurements, of the Joule-Thomson effect. Our own experience with a hydrogen liquefier is in good agreement with these curves.

COLUMBUS, OHIO

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

Joule-Thomson Effects in Deuterium at Liquid Air and at Room Temperatures¹

BY HERRICK L. JOHNSTON, CARROLL A. SWANSON AND HENRY E. WIRTH

In continuation of the program begun with hydrogen,^{1a} we have recently measured Joule-Thomson effects in pure deuterium. Measurements were made for pressures up to 190 atmospheres and for temperatures of 64, 69, 75, 80 and 298°K.

Purity of the Deuterium

The deuterium used was prepared by the electrolysis of 99.8% pure heavy water. The deuterium was collected in a small gas holder, over tri-cresyl phosphate as sealing fluid, and was stored under pressure in ordinary steel cylinders.

Oxygen contamination in the electrolytic gas was removed by passing the deuterium over platinized asbestos at 300°, and freezing out the water so formed in a liquid air trap through which the deuterium passed.

Nitrogen or air contamination was removed by passing the deuterium through charcoal at liquid air temperatures, under a pressure of 136 atmospheres. Frequent analyses for nitrogen were carried out in conjunction with the Joule-Thomson runs. For all except the 64° isotherm 0.2 of 1% was set as the maximum limit for impurity. When this limit was reached—due to nitrogen diffusion through the gas holder sealing fluid or due to entrance of air at any other part of the cycle—the gas was repurified before runs were continued. For the runs at 64°K., 0.05% was taken as the upper limit of impurity.

Tri-cresyl phosphate was selected as the gas holder sealing fluid because we have found, in another series of investigations, that the rate of diffusion of nitrogen through tri-cresyl phosphate is much lower than through oil. We have also in-

vestigated the rate of isotopic exchange between deuterium gas and tri-cresyl phosphate. In a period of two weeks deuterium which was stored over tri-cresyl phosphate in a small gas holder of the annular ring type (painted inside and out with aluminum paint) exchanged with hydrogen to the extent that the hydrogen content of the stored deuterium increased 0.32 of 1%—or about 0.02 of 1% per day. In the course of our measurements on deuterium, hydrogen contamination may have risen from the original 0.2 of 1% to as much as 0.5 of 1%. This should not be noticeable in the values obtained for the Joule-Thomson effects.

Modifications in the Cycle and in the Operating Conditions

For the Joule-Thomson measurements with deuterium we employed a Rix Type K Compressor in the cycle. This compressor has a normal delivery of 0.17 cubic meter per minute, when operating on hydrogen, and nearly all of our runs were taken with this flow rate through the valve. However, a few of the runs were made with a flow rate of 0.34 cubic meter per minute by putting a larger belt sheave on the motor. These are indicated by a footnote to Table I.

The use of tri-cresyl phosphate as gas holder sealing fluid has been mentioned. The gas holder was of the annular ring type, of fifteen cubic feet capacity and was constructed from tinned copper sheet with strap iron reinforcing.

One thousand pound and 3000 pound Crosby test gages, with 12-inch dials, were used to read the pressures, which were controlled manually. The gages were calibrated against a dead weight gage manufactured by the American Instrument Co. and calibrated by the U.S. Bureau of Standards. These gages replaced the 3000 pound turret gage with 3¹/₂" dial which was used in the measurements on hydrogen.

The most important changes were improvements in temperature control. The coil of 6.35 mm. o.d. copper tubing submerged in the liquid air, which had been reduced to 7.5 meters in the

(1) Presented before the Symposium on Low Temperature Research, at the Atlantic City meeting of the American Chemical Society, April 10, 1946.

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(1a) H. L. Johnston, Irving I. Bezman and C. B. Hood, *THIS JOURNAL*, **68**, 2367 (1946).

midst of the hydrogen runs, was restored to its original 15 meters length. Liquid nitrogen of 99% purity was substituted for liquid air, for most of the deuterium runs. Automatic vacuum regulation was installed on the evaporating liquid nitrogen. The most important of these changes is the use of liquid nitrogen as bath liquid, since this removed temperature irregularities caused by fluctuations in the composition of liquid air.

The automatic vacuum regulator, together with its connections into the system, is diagrammed in Fig. 1. The regulation consists, essentially, of bleeding dry air into the vacuum line leading from the cryostat whenever the vacuum improves beyond the regulator setting. By means of manually controlled valves the main vacuum line is opened up to the point that it will slowly improve the vacuum beyond the desired setting if bleeding is not resorted to, and valves on the bleeder line are set to allow slow bleeding sufficient to overcome the advantage of the vacuum pump, whenever the bleeder is opened. A mercury contact in the regulator responds to small changes in the cryostat pressure and operates a magnet which opens or closes the bleeder line. The regulator is quickly and conveniently set at any desired regulating pressure by opening the stopcock on the cross arm so as to equalize pressure in the two glass bulbs while the desired low pressure is established in the cryostat by manual operation of the valves. When the stopcock on the cross arm is closed so that the desired operating pressure is isolated in the closed off bulb, the regulator immediately functions at that pressure.

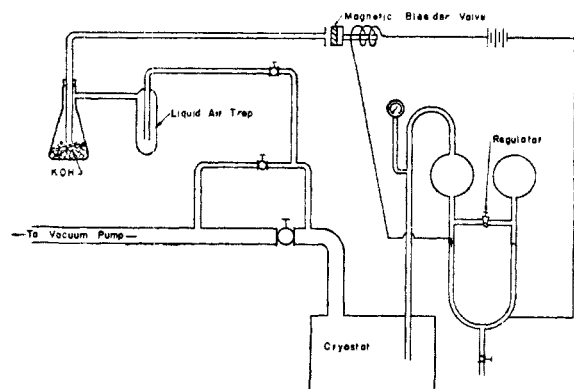


Fig. 1.—Vacuum regulator for automatic vacuum control on cryostat bath.

By proper adjustment of the hand-operated valves to obtain proper bleeding rates and proper evacuation rates, we obtained regulation to within 0.007 of an atmosphere or better. With liquid air in the cryostat this still permits considerable temperature fluctuation because of variation in the composition of the air as it vaporizes under reduced pressure. This necessitates careful control of the rate at which fresh liquid air is siphoned into the cryostat. With 99% liquid nitrogen the regulation is greatly improved and in many

of our runs—with the combination of the liquid nitrogen and of the vacuum regulator—the temperature of the cryostat bath has remained constant to within one or two microvolts for periods as long as forty-five minutes or an hour.

Experimental Results

Results are tabulated in Table I, and are shown graphically in Figs. 2 to 6 inclusive.

TABLE I

JOULE-THOMSON EFFECTS IN DEUTERIUM OVER THE PRESSURE RANGE 17 TO 204 ATMOSPHERES AND FOR INLET TEMPERATURES OF 64, 69, 75, 80 AND 298°K.

Run no.	Press. int. atm.	Inlet T, °K.	ΔT , °C.
1	17	64	- 4.80 ^{a,b}
2	17	69	- 3.90
3	34	64	- 9.86
4	34	69	- 8.18
5	34	75	- 6.73
6	17	75	- 3.24
7	51	64	-15.2 ^b
8	51	64	-14.88
9	51	69	-12.49
10	51	75	-10.00 ^b
11	68	75	-12.23
12	68	79	-15.62 ^b
13	68	79	-15.50
14	68	64	-19.02
15	85	64	-21.73
16	102	64	-23.58 ^b
17	102	69	-19.72 ^b
18	85	69	-17.86
19	85	75	-14.79
20	102	75	-16.49
21 (Lost)			
22	119	75	-17.58
23	119	69	-20.99 ^b
24	136	69	-21.36
25	198	64	-25.1 ^{a,b}
26	153	64	-25.62 ^a
27 (Lost)			
28 (Lost)			
29	170	64	-25.5 ^{a,b}
30	153	69	-21.59
31	170	69	-21.57
32	190	69	-21.72
33	136	75	-18.36
34	153	75	-18.72 ^b
35	119	64	-24.98
36	136	64	-25.57
37	190	75	-19.18
38	170	75	-19.22
39	170	64	-25.62
40	119	69	-21.23
41	190	64	-25.56
42	190	80	-16.75
43	170	80	-16.92
44	153	80	-16.80
45	17	80	- 3.45 ^{b,c}
46	136	80	-16.24
47	34	80	- 6.97 ^{b,e}

TABLE I (Concluded)

Run no.	Press. int. atm.	Inlet T, °K.	ΔT , °C.
48	17	80	- 2.98 ^{b,c}
49	34	80	- 5.60 ^a
50	17	80	- 2.89 ^{a,b}
51	51	80	- 8.28 ^a
52	(Discontinued)		
53	68	80	- 10.47 ^a
54	85	80	- 12.42 ^{a,b}
55	102	80	- 14.12 ^{a,b}
56	119	80	- 15.13 ^{a,b}
57	190	75	- 18.72
58	170	75	- 18.76
59	136	69	- 21.30 ^{b,d}
60	102	69	- 19.58 ^d
61	102	64	- 23.68 ^d
62	102	75	- 16.56 ^d
63	102	80	- 14.16 ^{a,b,d}
64	34	298	0.79 ^b
65	34	298	0.99 ^b
66	68	298	1.80 ^b
67	102	298	3.03
68	136	298	4.18
69	190	298	6.26
70	51	298	0.90
71	136	303	4.37 ^{b,e}

^a Liquid air was used as the thermostat bath for those runs marked by footnote ^a. All other runs used liquid nitrogen as thermostat bath. ^b Runs with somewhat unsteady readings or with fluctuations in readings due to unsatisfactory control of operating conditions. This footnote is indicated for every run in which individual readings of ΔT at five minute intervals showed deviations of more than a microvolt from the mean after sufficient time was allowed for attainment of thermal equilibrium. ^c Runs with footnote ^c are discarded because of high nitrogen contamination (several per cent.) that entered through a leak in the low pressure side of the cycle. ^d Runs with footnote ^d were made at flow rates of 0.34 cubic meter/min. All other runs were at 0.17 cubic meter/min. ^e This run was made at 30° to determine the temperature coefficient, for the purpose of applying small corrections to the other 25° runs to bring them to just 25°.

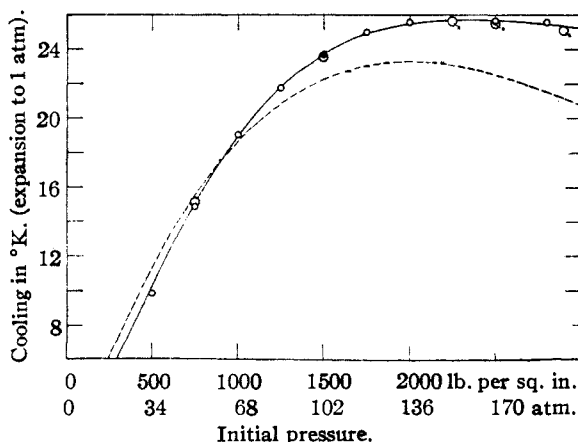


Fig. 2.—Joule-Thomson cooling in D₂ from an initial 64°K.: — smooth curve for D₂; --- H₂ curve; ●, points taken at 12 cfm. flow rate; ○, points taken at 6 cfm. flow rate; ○_A, points taken with liquid air rather than liquid N₂ as cryostat bath; ○, less reliable runs.

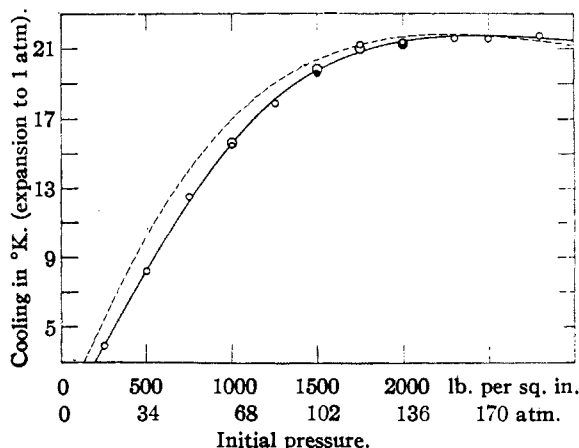


Fig. 3.—Joule-Thomson cooling in D₂ from an initial 69°K.: — smooth curve for D₂; --- H₂ curve; ○, points taken at 6 cfm. flow rate; ●, points taken at 12 cfm. flow rate; ○, less reliable runs.

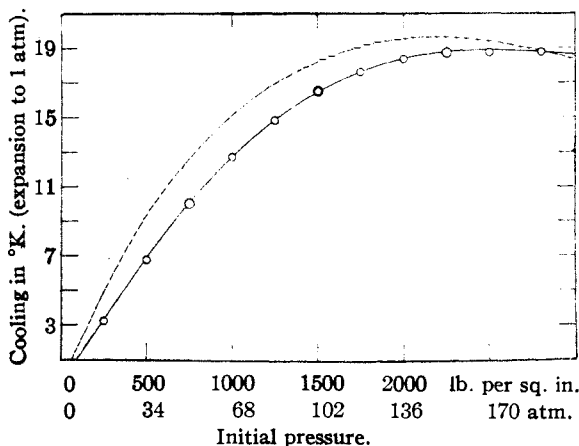


Fig. 4.—Joule-Thomson cooling in D₂ from an initial 75°K.: — smooth curve for D₂; ○, points taken at 6 cfm. flow rate; ●, points taken at 12 cfm. flow rate; ○, less reliable runs; --- H₂ curve.

As is apparent from Figs. 2 to 5 inclusive, the isotherms for deuterium possess maxima that lie between about 163 and 170 atmospheres. This is about 13 atmospheres higher than for hydrogen. The deuterium maxima are also somewhat flatter than those for hydrogen. Cooling effects at the several maxima are as follows: 25.7° for the 64° isotherm; 21.8° for the 69° isotherm; 19.9° for the 75° isotherm and 16.9° for the 80° isotherm. It is noteworthy that the 64° isotherm for deuterium lies well above that for hydrogen in the high pressure region but that it falls, relative to hydrogen, for the successively higher isotherms. For the 80° isotherm it is considerably below that of hydrogen. This implies that the virial coefficients for high powers of the pressure are larger for deuterium than for hydrogen but that the reverse must be true for virials of the lower pressure powers.

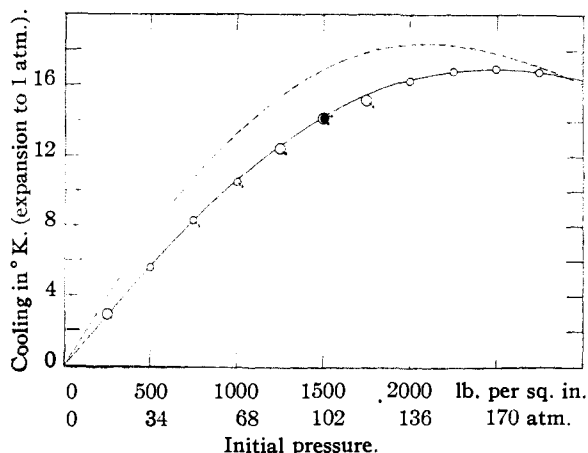


Fig. 5.—Joule-Thomson cooling in D_2 from an initial $80^\circ K.$: —smooth curve for D_2 ; --- H_2 curve; \circ , points taken at 6 cm. flow rate; \bullet , points taken at 12 cm. flow rate; \circ , less reliable runs; $\circ A$, liquid air as cryostat bath.

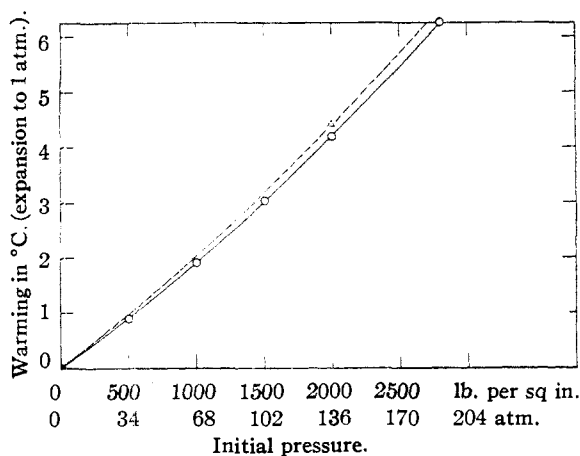


Fig. 6.—Joule-Thomson warming in D_2 from an initial 25° : — smooth curve for D_2 ; --- curve for H_2 at 25° (extrapolation from 15° measurements); \circ , experimental points at 25° ; \triangle , points at 30° .

Isobars are plotted in Fig. 7. From these, Joule-Thomson cooling effects readily may be interpolated or extrapolated, as functions of temperature.

Heat Contents of Deuterium as a Function of Pressure

We have computed values of $(H_0 - H_p)$ from the smoothed experimental curves of Figs. 2-6. The results are shown in Table II.

Acknowledgment.—We wish to acknowledge the assistance of Dr. W. E. Wallace, Mr. Cameron B. Satterthwaite, Mr. R. M. Haag, Mr. Aaron Greifer and Mr. Howard E. Brooks in taking data during the runs. We also wish to acknowledge the assistance of Dr. Irving I. Bezman in designing and assembling the vacuum regulator.

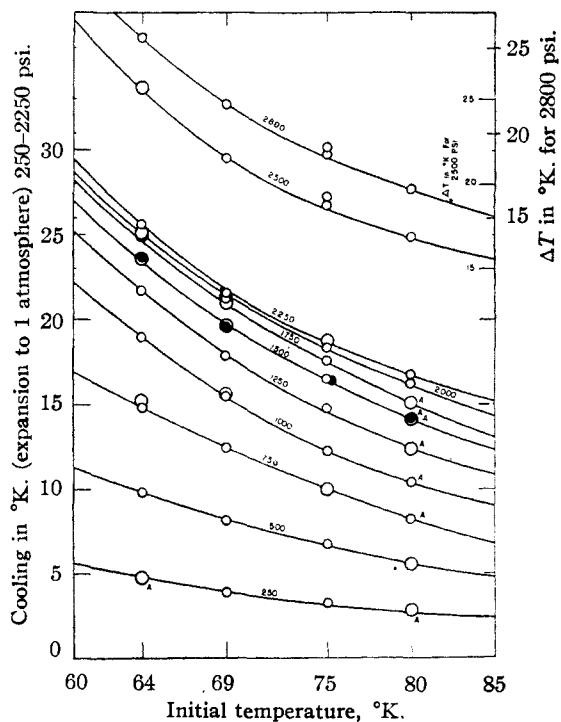


Fig. 7.—Isobars showing Joule-Thomson cooling in D_2 : \circ , experimental points at 6 cm.; \bullet , experimental points at 12 cm.; \circ , less reliable runs; $\circ A$, liquid air as cryostat bath.

TABLE II

MOLAR HEAT CONTENTS OF HYDROGEN, AS A FUNCTION OF THE PRESSURE, AT $25^\circ C.$ AND AT $80, 75, 69$ AND $64^\circ K.$, COMPUTED FROM OUR MEASURED JOULE-THOMSON EFFECTS

Press. lb./sq. in.	$H_p - H_0$ $25^\circ C.$	$H_0 - H_p$ $80^\circ K.$	$H_0 - H_p$ $75^\circ K.$	$H_0 - H_p$ $69^\circ K.$	$H_0 - H_p$ $64^\circ K.$
13.6	2.4	15.9	18.7	21.3	25.8
27.2	4.9	32.4	38.7	44.5	53.0
40.8	7.5	47.5	57.6	66.6	78.4
54.4	10.3	61.9	74.3	86.5	100.6
68	13.2	79.8	88.4	103.6	119.0
81.6	16.1	86.1	100.3	116.2	132.3
95.2	19.3	95.8	109.6	125.2	132.1
108.8	22.4	103.9	116.4	131.4	148.7
122.4	25.7	110.2	121.8	135.6	152.7
136	29.0	114.8	125.6	138.6	155.0
149.6	32.5	117.5	128.5	140.1	156.2
163.2	36.0	118.9	129.8	140.4	156.3
176.8	39.6	118.9	130.8	140.0	155.9
180.4	43.8	117.6	129.2	140.0	155.0
204	46.8	115.4	128.2	139.4	154.1

Summary

Joule-Thomson effects in deuterium have been measured for pressures up to 190 atmospheres and for isotherms at 64, 69, 75, 80 and $298^\circ K.$ Measurements were made with the apparatus described by Johnston and used previously to measure Joule-Thomson effects in hydrogen,¹ with some improvements in operating conditions—notably in temperature control.

Each of the low temperature isotherms exhibits a flat maximum at 163–170 atmospheres. The magnitudes of the Joule–Thomson cooling effects at the several maxima are as follows: 25.7° for the 64° isotherm; 21.8° for the 69° isotherm; 19.9° for the 75° isotherm and 16.9° for the 80° isotherm. The maxima are somewhat flatter than those observed for hydrogen. The 64° curve lies above that for hydrogen, in the high pressure region, but the relative positions of the curves is reversed for the 75 and 80° isotherms.

The 25° isotherm rises with a slight upward

inflection with an average Joule–Thomson coefficient of approximately 2.1° warming per 68 atmospheres of pressure drop.

A table of heat contents, as a function of pressure and of temperature, is computed from the smooth isotherms of our data.

The accuracy of the measurements made with deuterium exceeds that obtained with hydrogen. This is due principally to better temperature control obtained through the use of liquid nitrogen as cryostat bath liquid.

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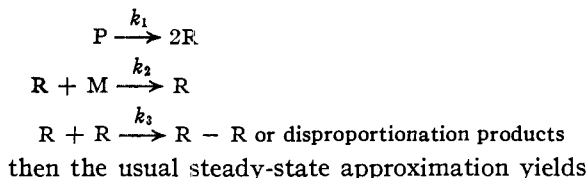
[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Rate Constants of the Steps in Addition Polymerization. I. The Induction Period in the Polymerization of Vinyl Acetate

BY KENZIE NOZAKI¹ AND PAUL D. BARTLETT

Introduction.—The term, “natural induction period,” used in this paper refers to the time required for the establishment of the steady state in a chain reaction. In an important paper in 1937, Flory² showed that for thermal polymerization the fractional conversion of the monomer to polymer at the end of the natural induction period is directly related to the ratio, k_3/k_2 , between the rate constants for chain termination and chain propagation in the scheme below.

Recent developments in the study of the chain-initiating process in peroxide-induced polymerization have raised the hope that the separate rate constants themselves might be evaluated, once the ratio k_3/k_2 was known. This follows from the fact that in all probability the rate of chain initiation is identical with the rate of spontaneous (as opposed to radical-induced) decomposition of the peroxide³ and therefore for peroxide-induced polymerization we have a direct way of measuring the rate of chain initiation, a way which does not exist in thermal or photochemical polymerization. If the steps in peroxide-induced polymerization are those of the following scheme, (R = radical, M = monomer, P = peroxide)



$$R = \sqrt{k_1 P / k_3} \quad (1)$$

and

$$\left(\frac{-dM}{dt} \right) / M = k_2 \sqrt{\frac{k_1 P}{k_3}} \quad (2)$$

(1) Pittsburgh Plate Glass Fellow, 1943–1945; present address, Shell Development Co., Emeryville, California.

(2) Flory, *THIS JOURNAL*, **59**, 241 (1937).

(3) Nozaki and Bartlett, *ibid.*, **68**, 1686 (1946).

The capital letters in the chemical equations denote molecular species, in the mathematical equations the concentrations of those species. The last combination of constants can be determined by a simple measurement of the rate of polymerization after the steady state has been reached. If this can be combined with an evaluation of k_3/k_2 from the measurement of the natural induction period, the two composites can be multiplied

$$\left(\frac{k_3}{k_2} \right) \left(k_2 \sqrt{\frac{k_1 P}{k_3}} \right) = \sqrt{k_1 k_3 P} \quad (3)$$

Since k_1 and P can both be determined experimentally, a direct evaluation of k_3 would thus be afforded, and accordingly an evaluation of k_2 as well. In a later section we show the necessary modifications of Flory's derivation to permit these calculations for peroxide-induced polymerization.

The possible utility of this method rests upon the crucial question of whether any instance of peroxide-induced polymerization has a measurable natural induction period or not. The lower the ratio k_3/k_2 , the longer is the natural induction period; therefore the most favorable case in which to measure this period would be the polymerization with the greatest kinetic chain length. We have chosen vinyl acetate for investigation and have found that the purest vinyl acetate is polymerized in the presence of benzoyl peroxide without any measurable induction period. This confirms indications reported by Bagdassarian.⁴

Experimental

Purification of Vinyl Acetate.—To determine the effect of the method of purification upon the rate of polymerization and the presence or absence of an induction period, four methods of purification and two methods of degassing were employed. The methods of purification were: A partial polymerization. Samples of vinyl acetate were heated with benzoyl peroxide until the mixture had be-

(4) Bagdassarian, *Acta Physicochim. U. R. S. S.*, **19**, 266 (1944).