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THE STATE DIAGRAM AND THE CRITICAL CONSTANTS OF AMYLENE.

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1. The State Diagram of Amylene.

Introduction.

The state diagram of 1-butene was reported in this journal[1]. The authors, therefore, have carried out the experiment on amylene, which is the same homologue having one more carbon in number. We have the compressibility data of amylene in its liquid state[2] in the narrow region, but no complete data in its gaseous state.

Apparatus and Procedure.

The apparatus used and the procedure were the same as in the preceding experiment. In the capillary tube (piezometer) used in the previous report, two pieces of platinum wire were sealed at the same position. Therefore, there was a disadvantage of leaving mercury on the platinum wire, and making the measurement of the volume incorrect. In this experiment, a single piece of wire was sealed alternatively at each contact except at the first contact point.

Sample.

Amylene was prepared from isoamylalcohol (B. P. 125~130°C), which was dehydrated* and then carefully distilled by means of the Podbielniak fractionating apparatus. The distillation curve is shown in Fig. 1, where it is seen that three kinds

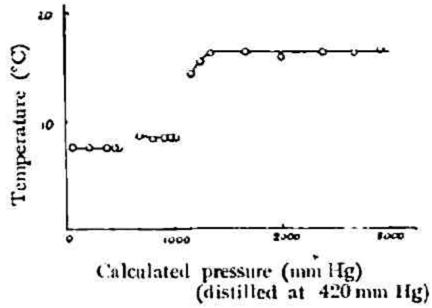

Fig. 1

1) R. Kiyama and H. Kinoshita, *This Journal*, 19, 43 (1943)

2) W. A. Suchodski, *Z. Phys. Chem.*, 74, 257 (1910)

* The catalyser of alcohol dehydration and the conditions were the same as in the case of butene in the previous work.

of isomer are contained in the distillate. In the present experiment was used iso-amylene (2–methylbutene-2) having the highest boiling point, 37.8°C (760 mm Hg)*.

Results.

Summarizing these results obtained, we assumed amylene gas under 1 atm to follow the ideal gas law at each temperature. The results are shown in Tables 1 and 2, and graphically in Fig. 2**.

Table 1

Measurements (i): The gas sample, 3,730 cc at 544.0 mm Hg, 27.9°C.

a) 150°C

Patm	V*	Vl/mol	PV	Phase
1.0	1.551		1.551	Gas
12.4	1.101	2.270	1.255	"
13.7	0.0844	1.891	1.159	"
14.4	0.0672	1.505	0.954	Gas & Liquid
14.4	0.0511	1.146	0.727	"
14.4	0.0337	0.754	0.478	"
14.4	0.0164	0.367	0.238	"

b) 165°C

Patm	V	Vl/mol	PV	Phase
1.0	1.606		1.606	Gas
13.3	1.101	2.270	1.343	"
15.2	0.0844	1.891	1.282	"
17.4	0.0672	1.505	1.170	"
18.5	0.0511	1.146	0.945	"
18.8	0.0337	0.754	0.632	Gas & Liquid
18.8	0.0164	0.367	0.308	"

c) 175°C

Patm	V	Vl/mol	PV	Phase
1.0	1.642		1.642	Gas
13.8	0.101	2.270	1.402	"
15.7	0.0844	1.891	1.323	"
18.2	0.0672	1.505	1.222	"
20.7	0.0511	1.146	1.059	"
21.2	0.0337	0.754	0.713	Gas & Liquid
21.2	0.0164	0.367	0.347	"

* Regarding the boiling points of the isomers, there is a difference in various tables. After G. Egloff, "*Physical Constants of Hydrocarbons*," Vol. 1 (1939):
3–methylbutene-1 20.1°C, 2–methylbutene-2 38.6°C, 2–methylbutene-1 31°C.

** The experimental errors were ±0.2°C, 1/3 atm, 1/5000 volume.

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d) 185°C

Patm	V	Vl/mol	PV	Phase
1.0	1.679		1.679	Gas
14.2	0.101	2.270	1.441	"
16.6	0.0844	1.891	1.404	"
19.6	0.0672	1.505	1.319	"
23.0	0.0511	1.146	1.178	"
24.7	0.0337	0.754	0.830	Gas & Liquid
24.7	0.0164	0.367	0.404	"

e) 195°C

Patm	V	Vl/mol	PV	Phase
1.0	1.716		1.716	Gas
15.0	1.101	2.270	1.519	"
17.1	0.0844	1.891	1.445	"
20.1	0.0672	1.505	1.352	"
24.0	0.0511	1.146	1.228	"
28.0	0.0337	0.754	0.941	Gas & Liquid
28.0	0.0164	0.367	0.458	"

f) 210°C

Patm	V	Vl/mol	PV	Phase
1.0	1.770		1.770	Gas
15.5	1.101	2.270	1.568	"
18.0	0.0844	1.891	1.519	"
21.3	0.0672	1.505	1.430	"
25.5	0.0511	1.146	1.302	"
30.6	0.0337	0.754	1.029	"
33.9	0.0164	0.367	0.555	"

g) 230°C

Patm	V	Vl/mol	PV	Phase
1.0	1.844		1.844	Gas
16.6	0.101	2.270	1.686	"
19.8	0.0844	1.891	1.674	"
23.0	0.0671	1.505	1.547	"
27.6	0.0511	1.146	1.411	"
34.6	0.0337	0.754	1.166	"
42.8	0.0164	0.367	0.701	"

* The volume at 0°C, 1 atm was taken as unit.

The critical temperature was found between 195~200°C from the measurements in the neighbourhood of 200°C.

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Table 2

Measurements (ii): The gas sample, 5.667 cc at 551.1 mm Hg, 29.2°C.

a) 150°C

Patm	V	Vl/mol	PV	Phase
1.0	1.551		1.551	Gas
14.4	0.0661	1.481	0.939	Gas & Liquid
14.4	0.0550	1.234	0.782	"
14.4	0.0438	0.982	0.623	"
14.4	0.0334	0.748	0.474	"
14.4	0.0220	0.492	0.312	"
14.4	0.0107	0.240	0.152	"

b) 165°C

Patm	V	Vl/mol	PV	Phase
1.0	1.606		1.606	Gas
17.6	0.0661	1.481	1.164	"
18.8	0.0550	1.234	1.033	Gas & Liquid
18.8	0.0438	0.982	0.823	"
18.8	0.0334	0.748	0.627	"
18.8	0.0220	0.492	0.412	"

c) 175°C

Patm	V	Vl/mol	PV	Phase
1.0	1.642		1.642	Gas
18.3	0.0661	1.481	1.209	"
20.1	0.0550	1.234	1.108	"
21.2	0.0438	0.982	0.929	Gas & Liquid
21.2	0.0334	0.748	0.707	"
21.2	0.0220	0.492	0.465	"
21.2	0.0107	0.240	0.227	"

d) 185°C

Patm	V	Vl/mol	PV	Phase
1.0	1.679		1.679	Gas
19.7	0.0661	1.481	1.305	"
21.7	0.0550	1.234	1.193	"
24.3	0.0438	0.982	1.064	"
24.6	0.0334	0.748	0.820	Gas & Liquid
24.6	0.0220	0.492	0.540	"

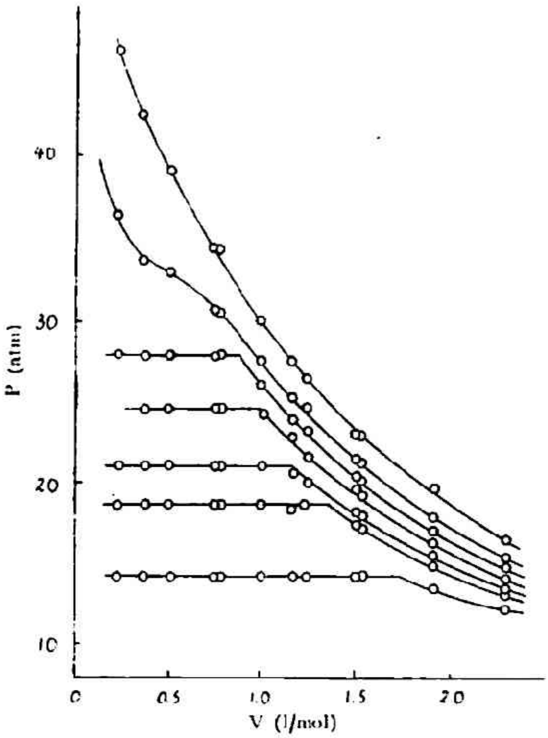

Fig. 2

e) 195°C

Patm	V	Vl/mol	PV	Phase
1.0	1.716		1.716	Gas
20.6	0.0661	1.481	1.362	,,
23.1	0.0550	1.234	1.273	,,
26.1	0.0438	0.982	1.145	,,
28.0	0.0334	0.748	0.933	Gas & Liquid
28.0	0.0220	0.492	0.614	,,
28.0	0.0107	0.240	0.299	,,

f) 210°C

Patm	V	Vl/mol	PV	Phase
1.0	1.771		1.771	Gas
21.5	0.0661	1.481	1.420	,,
24.6	0.0550	1.234	1.353	,,
27.7	0.0438	0.982	1.213	,,
30.8	0.0334	0.748	1.027	,,
33.1	0.0220	0.492	0.727	,,
36.7	0.0107	0.240	0.392	,,

g) 230°C

Patm	V	Vl/mol	PV	Phase
1.0	1.844		1.844	Gas
23.2	0.0661	1.481	1.541	"
26.3	0.0550	1.234	1.449	"
30.1	0.0438	0.982	1.319	"
34.6	0.0334	0.748	1.156	"
39.4	0.0220	0.492	0.865	"
46.9	0.0107	0.240	0.502	"

2. The Critical Constants of Amylene.

Introduction.

We determined previously the state diagram of amylene, and then found the critical temperature being between 195~200°C. But the fluid having a very large compressibility in the neighbourhood of the critical point, we must make a measurement apparatus so high in accuracy in order to determine the critical constant directly from the isothermal line. The apparatus which we used for measuring the P-V-T relation is not adequate for the present purpose. Then, we gained the critical constant of amylene from measurement for the critical phenomena, which has been generally made since Andrews.

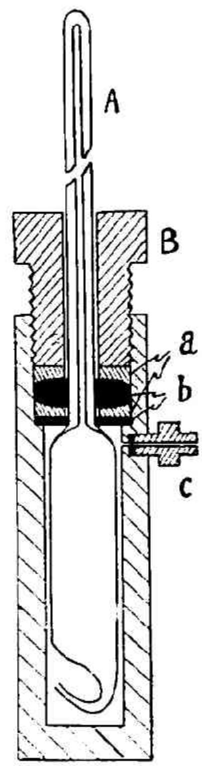

Fig. 3

Apparatus and Procedure.

The measurement apparatus consists of the glass vessel A and the steel pressure bomb B as is shown in Fig. 3. The upper part of A is made of the thick glass tube, which is 7 mm in the outer diameter and 1 mm in the inner diameter and anealed to take off the strain before use. The lower part of A is served as a gas holder. This thick glass tube was safe to 200°C, a few hundred atm. In the steel pressure bomb **a** is a steel ring, **b** a hard rubber packing. The part **c** is connected to the Cailletet pump and the pressure gauge through the metal tube. It is possible to measure up to about 100 atm in use of this apparatus. The pressure gauge used is of Burdon type. The degree of the scale is 1/3 kg/cm². The procedures of sampling or by which the sample is put in the apparatus are the same as in the previous report. Thus A is set into B filled with mercury. Heating of the thick glass tube A is done in the air bath with a long narrow glass window. The measurement of the temperature is made by means of mercury thermometer. The degree of the scale is 0.2°C. Such preparatory procedures as stated above are followed by the measurement of the critical point*.

We determine the point as critical at which the meniscus suddenly disappears, with a slow rise of temperature.

Moreover, a careful attention should be paid for the equilibrium of the temperature because the thick glass tube is used. We obtain the difference between the outer and the inner temperatures in the glass tube (thickness, 3.5 mm, the diameter of the bore, 4 mm) filled with the oil with rise of temperature in the same manner as in the measurement of the critical point. From the results the outer and the inner temperatures are found to be equal**.

Results.

According to the above procedure, we obtained 197.2°C and 33.7 atm as the critical temperature and pressure respectively. The critical temperature was between 195~200°C from the results of the state diagram of amylene obtained previously. Accordingly, both results coincide. Comparing with the critical constants of amylene already obtained, we have the following table.

	B. P.	T_c(obs.)	T_c(cal.)	P_c	Literature
amylene	40	201.2	202	—	McKee & Parker[3]
i-amylene	36	191.5	197	—	"
"	—	191.6	—	33.9	Nadejdine[4]
"	37.8	197.2	199.7	33.7	Authors

McKee and Parker have proposed the following relation between the boiling

* From the result that temperature in the disappearance of the meniscus is influenced by the thermal history of the material, O. Maass has defined the critical temperature as follows: it is the temperature when the meniscus diminishes with rising temperature after the material has been cooled below 1°C at least lower the critical temperature beforehand (*Phil. Trans.*, 236, 303 (1937): *Chem. Rev.*, 23, 17 (1938)).

** The difference between the inner and the outer temperatures is observed by the copper-constantan thermocouple.

3) R. H. McKee and H. H. Parker, *Ind. Eng. Chem.*, 20, 1169 (1928)
4) *Landolt-Börnsteins Tabellen*, 255 (1923)

point and the critical temperature of hydrocarbon,

$$t_c = 1.05t_b + 160,$$

where t_c is the critical temperature and t_b is the boiling point. Substituting the value of the boiling point, 37.8°C of the sample used, we have 199.7°C as the critical temperature. The comparison with the results of McKee and Parker is shown in the above table.

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