STATE DIAGRAM OF STEAM

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Introduction

Formerly, the state diagrams of steam above critical temperature have been obtained by Nieuwenburg[1], Keyes and Smith[2], Kennedy[3] and Kirillin[4]. The highest temperatures and pressures in each author were as follows, Nieuwenburg, 477.5°C, 600 kg/cm²: Keyes and Smith, 460°C, 360 atm: Kennedy, 1000°C, 2500 bar: Kirillin, 600°C, 524 atm respectively. Keyes derived the equation of state by using his experimental data[5]. Since their values being fairly different from each other the re-experimentation was considered to be necessary, so that the authors measured the P-V-T relations of steam at the same conditions and examined which value would be coincident with ours.

Experimentals

The apparatus used is the simple one which is used in the experiment of the equilibrium of urea and water[6] and previously the state diagram of benzene-methanol mixture was obtained by this apparatus[7]. The experimental conditions are as follows: temperatures are 380, 400, 420, 440 and 460°C, specific volumes are between 10 and 1.45 cc/g and the pressure up to 820 atm, and the experimental results are compared with the values of the above several authors.

Experimental procedures of the present authors are the method of constant volume, namely a given quantity of water is inspired in an autoclave through a valve and the pressures are determined at several temperatures to a definite specific volume. The pressures are determined by the pressure gauge of Bourdon type, which is separated by mercury from autoclave. On the other hand, the way of Nieuwenburg is the same as

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2) F. G. Keyes and L. B. Smith, *Mech. Eng.*, **53**, 132 (1931); **54**, 123 (1932)
F. G. Keyes, *Proc. Am. Acad. Arts Sci.*, **68**, 505 (1933)
3) G. C. Kennedy, *Am. J. Sci.*, **248**, 540 (1950)
4) W. A. Kirillin and L. L. Rumjanzev, *Elektrischeskije Sstanzii*, **21**, 8 (1950)
5) F. G. Keyes, *J. Chem. Phys.*, **17**, 923 (1949)
6) R. Kiyama and H. Kinoshita, *This Journal*, **21**, 9 (1951)
7) H. Kinoshita and K. Shimizu, *ibid.*, **23**, 35 (1953)

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that of the authors except that the pressure gauge is not separated by mercury from autoclave and so the quantity of condensed water in pressure gauge is subtracted from the quantity of the water used. The way of Kennedy is the same as used by Keyes—— the water is introduced into the autoclave by the compressor of screw driven type and the relations between pressure and volume are obtained. The autoclave of the authors is made with Ni-Cr-steel, the capacity of which is about 35 cc. The composition of this steel is given in Table 1 and the decomposition of water did not occur in experimental conditions.

Table 1

	C	Ni	Cr	Mo	Cu	W	Co	Cb
Authors	0.08	21.24	17.39	1.64	1.87			
Kennedy	1	30	20	3		2	20	1
Keyes	0.15	8	18					

The pressure gauges used are 500 and 1000 kg/cm^2 in maximum scale and the maximum errors are ± 1.5 and ± 3 kg/cm^2 respectively.

Results

The experimental results are shown in Table 2 and Figure with the values of P and PV/RT, and the values of Nieuwenburg, Kennedy and those calculated from the equation of Keyes are also plotted.

The results of the authors are in accordance with the values of Kennedy at the experimental range of each specific volume at 460°C and slightly deviated at the specific

Table 2

380°C		400°C		420°C		440°C		460°C	
P atm	$\frac{PV}{RT}$	P atm	$\frac{PV}{RT}$	P atm	$\frac{PV}{RT}$	P atm	$\frac{PV}{RT}$	P atm	$\frac{PV}{RT}$
181	0.608	197	0.641	211	0.668	226	0.694	240	0.719
205	.517	227	.554	249	.591	269	.621	289	.650
217	.456	244	.497	271	.537	295	.568	320	.600
226	.379	261	.426	294	.466	328	.505	360	.539
230	.348	268	.394	305	.435	343	.475	378	.506
234	.315	277	.361	319	.405	363	.447	403	.482
234	.276	283	.323	335	.371	385	.415	431	.451
240	.242	297	.291	358	.340	417	.385	469	.422
251	.211	322	.263	394	.312	464	.357	533	.399
259	.196	346	.254	427	.304	507	.351	590	.398
266	.190	362	.251	447	.301	535	.350	630	.401
276	.185	376	.248	479	.304	585	.360	689	.413
300	.192	415	.257	520	.313	635	.371	747	.425
337	.204	460	.270	577	.329	699	.387	820	.442
392	.224	527	.292	662	.357	790	.413		
484	.260	645	.336	780	.395				
646	.326	819	.401						
749	.365								

$R = 0.0820566$ liters atm/degree, V = liters/mole

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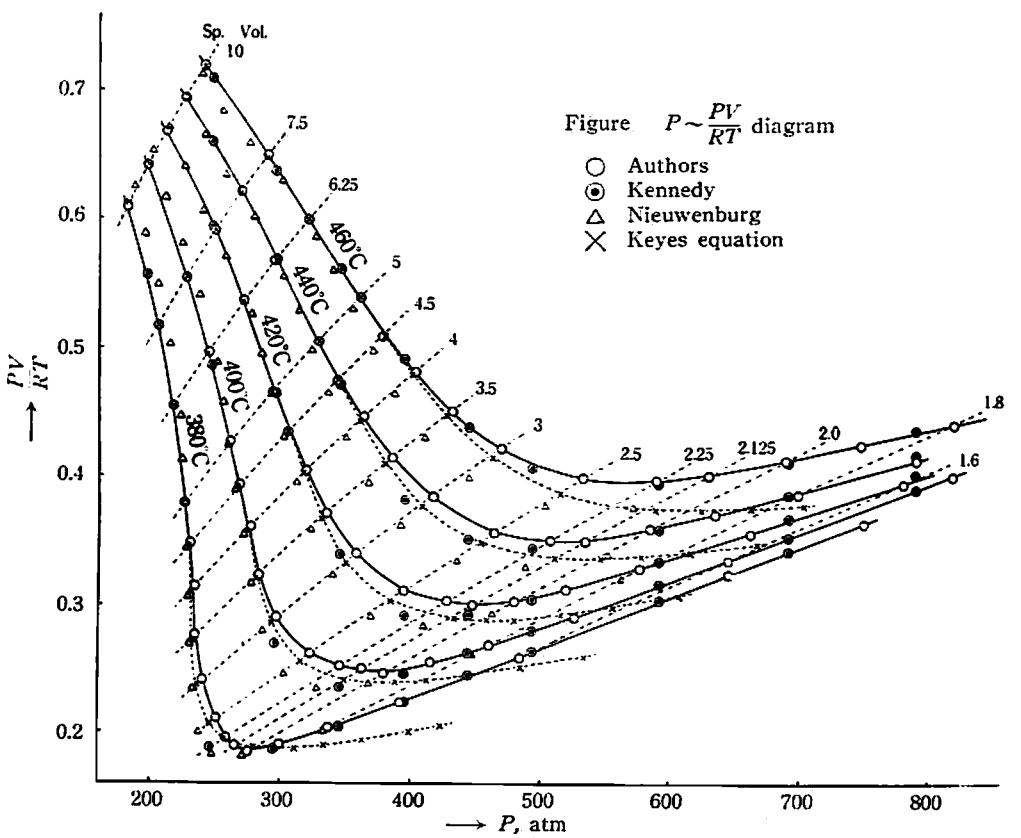
volumes 2～4 at 380～440°C. The maximum difference of pressures at the same specific volume between the authors and Kennedy is about 20 atm and the values of the authors are higher than those of Kennedy. And the results of the authors are in accordance with the values of Nieuwenburg at the specific volumes of about 6～7 and 1.8, and fairly differ except the above specific volumes. The maximum difference is about 30 atm and the values of the authors are higher than those of Nieuwenburg. And the values calculated from the equation of state of Keyes which is derived from the results of the specific volumes of above 5, are in accordance with the results of the authors at the specific volumes of above 2 at 380°C and above 4 at 400～460°C, but extremely differ below these specific volumes.

On the other hand, the values of Kennedy are in accordance with the values of Nieuwenburg at the specific volume of about 2 at 380～420°C and about 6 at all temperatures. And those of Kennedy are in accordance with the calculated values of Keyes at the specific volumes of above 4 at 460°C and above 3 at 440～380°C. The calculated values of Keyes are in accordance with the values of Nieuwenburg at the specific volumes of about 6 and 2 at 380～440°C.



From the above considerations, at the specific volumes of above 5, the values of several authors are almost coincident to each other, but at the specific volumes of below 5, the results of authors are fairly in accordance with the values of Kennedy, and the values of Nieuwenburg and the calculated values of the equation of Keyes fairly differ from the values of the authors and Kennedy, so the values of the authors and Kennedy may be preferable.

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