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ON THE THERMODYNAMIC PROPERTIES OF ACETYLENE UNDER HIGH PRESSURES

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Introduction

With the development of acetylene chemistries, it has become necessary to have some knowledge on the thermodynamic properties of acetylene for handling it under high pressures. Nevertheless, these properties under high pressures have not yet been reported in detail. Sameshima¹⁾ and Rimarski²⁾ investigated the *P–V–T* relations of acetylene and, however, their measurements were limited in the narrow ranges of temperature (0 ~ 25°C) and pressure (0.5 ~ 20 atm). The van der Waals equation of state for acetylene* which was computed from these data shows more than 50% deviation in the value of volume under even 50 atm, and can scarcely serve as the basis for the evaluations of other thermodynamic properties of acetylene under high pressures.

In our laboratory, the *P–V–T* relations of acetylene were measured by Kiyama, Ikegami and Inoue over the wide ranges of temperature (−8 ~ 250°C) and pressure (11 ~ 145 atm), and the method and results of the measurements were reported schematically in 1951³⁾. In the present paper, the author will mention in detail the *P–V–T* relations of acetylene which are estimated, on the basis of above-mentioned measurements, by the inter- and extrapolation of the temperature and pressure and by making the sufficient corrections for the volume and especially for the critical conditions, and will report the thermodynamic properties of acetylene under high pressures which have been evaluated from the *P–V–T* values.

P–V–T Relation

Several methods have been reported⁴⁾ on the correction of *P–V–T* relation of a gas and on the estimation of some other thermodynamic properties of the gas from the

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* $(P+4.39/V^2)(V-0.0514)=RT$ (atm liters/mole),
I. M. Klotz, *Chemical Thermodynamics*, P. 69, Prentice-Hall, Inc., New York, 1950

1) J. Sameshima, *Bull. Chem. Soc. Japan*, **1**, 41 (1926)

2) W. Rimarski and M. Konschak, *Autogene Metallbearbeitung*, **26**, 129 (1933)

3) R. Kiyama, T. Ikegami and K. Inoue, *This Journal*, **21**, 58 (1951)

4) A. Michels *et al.*, *Physica*, **3**, 569, 597 (1936); *Proc. Roy. Soc.*, **A153**, 201, 214 (1936); **A160**, 376 (1937); *App. Sci. Res.*, **1**, 94, 103 (1948)
W. C. Edmister, *Ind. Eng. Chem.*, **28**, 1112 (1936); **30**, 325 (1938)
S. H. Maron and D. Turnbull, *Ind. Eng. Chem.*, **34**, 544 (1942); *J. Am. Chem. Soc.*, **64**, 44 (1942)
J. R. Roebuck and H. Osterberg, *Phys. Rev.*, **45**, 332 (1934); **48**, 450 (1935)

P-V-T relation. Although the residual volume method of Deming and Shupe[5] is most laborious among them, yet it is thought to be most accurate in its results of estimation. The residual volumes Δ and α are defined as follows:

$$\Delta \equiv V\left(\frac{PV}{RT}-1\right), \tag{1}$$

$$\alpha \equiv \frac{RT}{P}-V. \tag{2}$$

In the residual volume method, Δ or α is computed from the data of P-V-T measurements and plotted against pressure and temperature, and then reasonable smoothed lines of Δ or $\alpha \sim P$ isotherms and Δ or $\alpha \sim T$ isobars are determined. The volume at desired pressure and temperature is evaluated readily from the value of Δ or α at the conditions and determined so that the reasonable coincidence has been found in its two values which are evaluated from both Δ value and α value.

The basic P-V-T relations in which the postulation that the acetylene gas follows the ideal gas law at 1 atm and each temperature is assumed are measured on acetylene of 99.3% purity at several points of pressure between 11.40 and 145.30 atm on every isotherms of −8.0, 0.1, 20.5, 30.3, 40.0, 52.4, 60.5, 72.5, 79.5, 100.0, 150.5, 200.0, and 250.0°C.

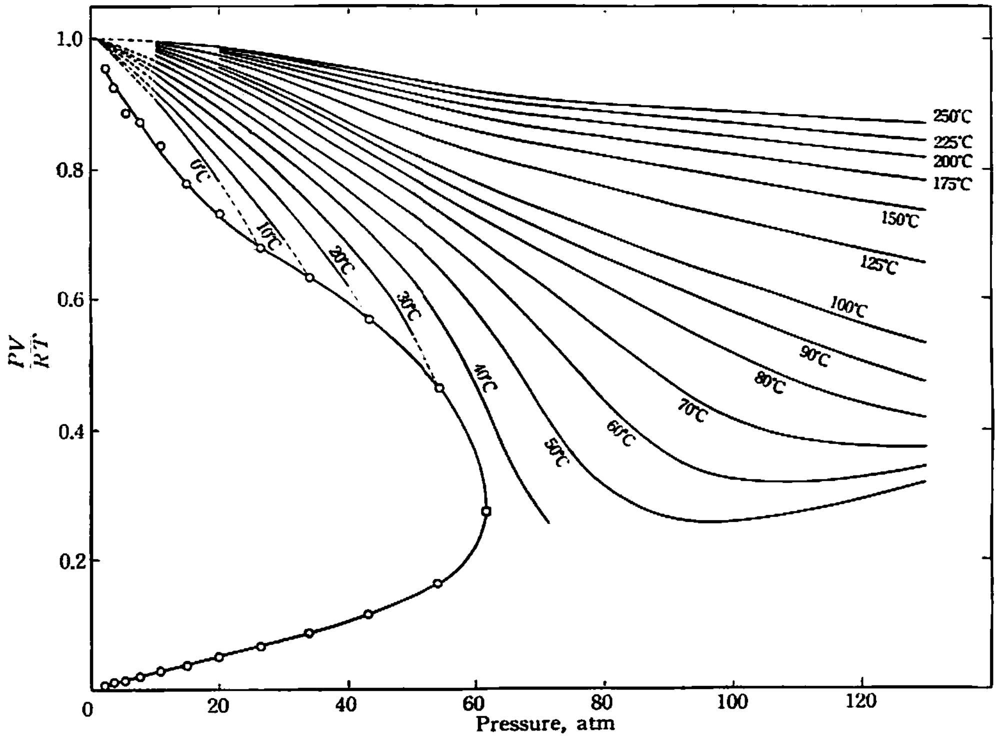

Fig. 1 $PV/RT \sim P$ isotherms of acetylene
○: calculated from the vapor pressure data

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[5] W. E. Deming and L. E. Shupe, *Phys. Rev.*, 37, 638 (1930); 38, 2245 (1931); 40, 848 (1932)

Table 1 *P*-*V*-*T* relation of acetylene
(*V* : liters/mole)

T, °C	*P*, atm	10	20	30	40	50	60	70	80	90	100	110	120	130
250	*V*	4.279	2.120	1.392	1.025	0.805	0.659	0.558	0.484	0.427	0.382	0.345	0.314	0.287
	PV/RT	0.997	0.988	0.973	0.955	0.937	0.921	0.910	0.902	0.896	0.891	0.884	0.876	0.869
225	*V*	4.073	2.014	1.319	0.969	0.759	0.620	0.525	0.455	0.401	0.357	0.321	0.291	0.266
	PV/RT	0.996	0.986	0.968	0.948	0.928	0.910	0.898	0.890	0.882	0.873	0.864	0.854	0.844
200	*V*	3.866	1.908	1.246	0.912	0.712	0.581	0.490	0.424	0.372	0.331	0.297	0.268	0.244
	PV/RT	0.996	0.983	0.963	0.940	0.917	0.898	0.884	0.873	0.862	0.852	0.841	0.828	0.817
175	*V*	3.658	1.801	1.172	0.854	0.665	0.541	0.455	0.391	0.342	0.303	0.271	0.244	0.221
	PV/RT	0.995	0.979	0.956	0.929	0.904	0.882	0.866	0.852	0.837	0.824	0.810	0.796	0.782
150	*V*	3.450	1.693	1.096	0.795	0.614	0.497	0.417	0.357	0.310	0.273	0.243	0.218	0.196
	PV/RT	0.994	0.975	0.947	0.916	0.884	0.860	0.840	0.822	0.804	0.787	0.769	0.752	0.735
125	*V*	3.241	1.584	1.019	0.733	0.562	0.451	0.373	0.315	0.271	0.236	0.208	0.184	0.164
	PV/RT	0.992	0.969	0.935	0.898	0.860	0.827	0.799	0.772	0.747	0.723	0.699	0.676	0.654
100	*V*	3.031	1.471	0.938	0.667	0.505	0.398	0.323	0.268	0.226	0.193	0.166	0.143	0.125
	PV/RT	0.990	0.961	0.919	0.872	0.825	0.780	0.738	0.700	0.664	0.629	0.595	0.562	0.530
90	*V*	2.946	1.424	0.905	0.640	0.481	0.376	0.301	0.247	0.206	0.173	0.147	0.125	0.108
	PV/RT	0.988	0.956	0.911	0.860	0.808	0.756	0.708	0.664	0.621	0.580	0.541	0.505	0.473
80	*V*	2.858	1.375	0.869	0.611	0.457	0.353	0.279	0.224	0.182	0.150	0.125	0.106	0.093
	PV/RT	0.986	0.949	0.900	0.844	0.788	0.730	0.673	0.618	0.566	0.517	0.474	0.439	0.418
70	*V*	2.765	1.321	0.831	0.580	0.430	0.327	0.251	0.192	0.146	0.118	0.099	0.088	0.081
	PV/RT	0.982	0.939	0.885	0.825	0.764	0.697	0.624	0.546	0.468	0.418	0.387	0.374	0.374
60	*V*	2.665	1.264	0.790	0.547	0.399	0.297	0.216	0.151	0.109	0.088	0.079	0.075	0.072
	PV/RT	0.975	0.925	0.866	0.800	0.730	0.652	0.552	0.443	0.358	0.323	0.318	0.328	0.343
50	*V*	2.563	1.205	0.746	0.511	0.364	0.257	0.163	0.103	0.078	0.068	0.066	0.065	0.065
	PV/RT	0.967	0.909	0.844	0.770	0.687	0.582	0.431	0.311	0.265	0.257	0.273	0.296	0.320
40	*V*	2.460	1.145	0.701	0.471	0.324	0.198	0.100	0.047					
	PV/RT	0.957	0.891	0.818	0.734	0.631	0.463	0.273	0.146					
30	*V*	2.356	1.083	0.653	0.428	0.269								
	PV/RT	0.947	0.870	0.788	0.688	0.541								
20	*V*	2.250	1.017	0.600	0.373									
	PV/RT	0.935	0.846	0.748	0.620									
10	*V*	2.143	0.949	0.536										
	PV/RT	0.922	0.817	0.692										
0	*V*	2.035	0.873											
	PV/RT	0.908	0.779											

The values of critical constants which were reported previously[3] seem to have some errors due to the impurity of 0.7% contained in the gas and the difficulty in determining the critical values and, therefore, in the present estimation, the most reasonable values reported in literature[6] are used for the critical constants and they are shown in the next table together with the fundamental numerical constants which are employed in the calculation.

$C_2H_2 = 26.036$	$P_c = 61.6$ atm
$0°C = 273.16°K$	$t_c = 36.0°C$
$R = 0.0820544$ liters atm/deg	$V_c = 113$ cc/ mole
1 liter atm $= 24.2179$ cal/mole	$\rho_c = 0.231$ g/cc

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[6] K. A. Kobe and R. E. Lynn, Jr., *Chem. Rev.*, 52, 117 (1953)

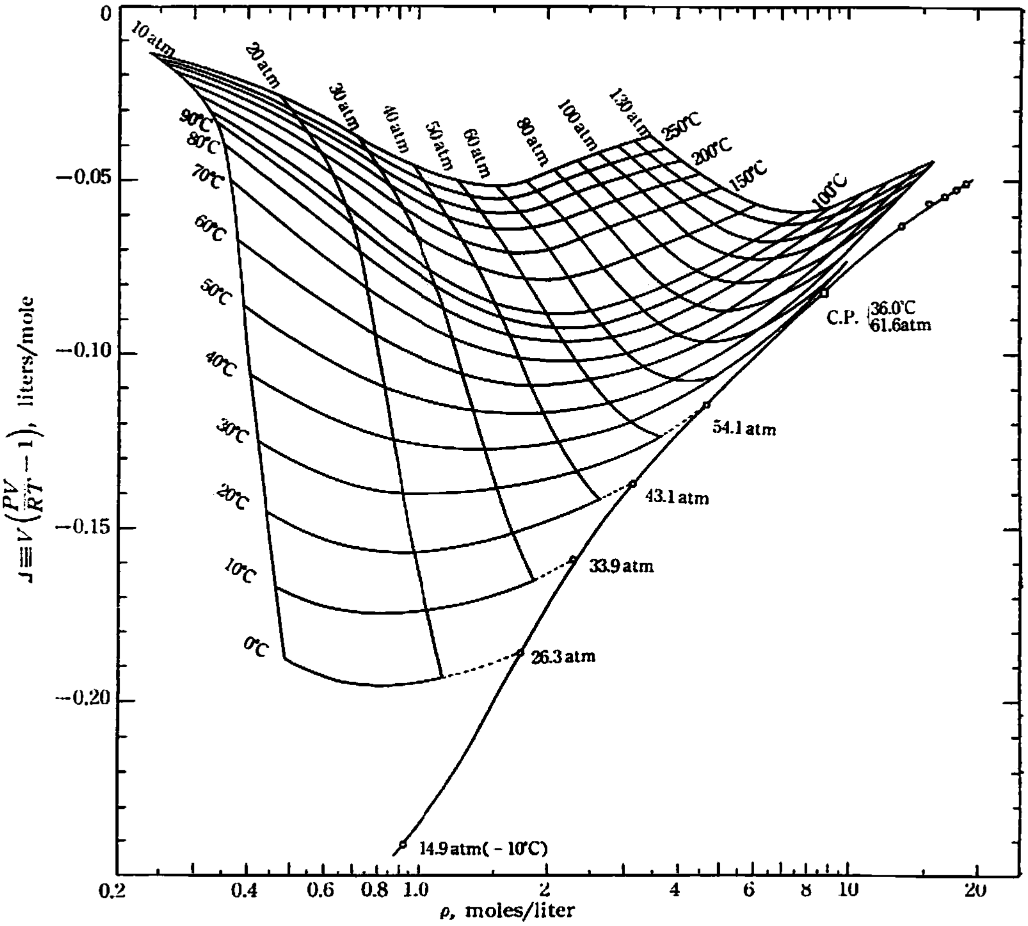

Fig. 2 $\Delta \sim \rho$ isotherms and isobars of acetylene
○ : calculated from the vapor pressure data

The results of the estimation of V and PV/RT in the ranges of 0 ~ 250°C and 10 ~ 130 atm are tabulated in Table 1, and $PV/RT \sim P$ isotherms and $\Delta \sim \rho$ isotherms and isobars are shown in Fig. 1 and Fig. 2 respectively. The values corresponding to sign ○ in Figs. 1 and 2 are calculated from the data on the vapor pressures of acetylene listed in International Critical Tables7) and show good coincidence to the extrapolated lines of respective isotherms of the present results.

In the basic data of P-V-T relations, the errors of the measurements of temperature, pressure and volume are ±0.05°C, ±0.017 ~ 0.05 atm and $\pm 2\times10^{-3}$ liters/mole respectively and the relative errors of the volume (0.16 ~ 1.8%) are most effective in the errors of the PV/RT except that at the minimum pressure in the measurements (11.40 atm) where relative error of the volume is comparable to that of pressure. In the present correcting procedure, the smoothed lines of every isotherms and isobars of Δ and α have

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7) *Inter. Crit. Tables*, 3, P. 230

been corrected reasonably so that the two values of the volume under any desired condition which are evaluated from both Δ and α values respectively coincide within 0.001 liters/mole, i. e. the half of the errors of volume in the basic measurements, and therefore, each value of volume listed in Table 1 has the error of ±0.001 liters/mole and the relative errors of PV/RT are calculated, by the least square method[8], to be 0.09 ~ 0.9%. Owing to the postulation in the basic data, the results of the present estimation have also the postulation that the acetylene gas under 1 atm obeys the ideal gas law at each temperature. If the real values of volume of acetylene under the standard condition (0°C, 1 atm) and its thermal expansion coefficients at 1 atm reported until the present** are used instead of the ideal behaviors, the values of volume in Table 1 have 0.86, 0.72, 0.30, and 0.07% deviations at 0°, 10°, 100°, and 250°C respectively.

Thermal Expansion Coefficient at Constant Pressure

Generally it is almost impossible to obtain the accurate $(dV/dT)_p$ values from the slopes of $V \sim T$ isobars, because the latter are nearly straight lines except at the conditions near the critical point and liquefying points. On the other hand, it is comparatively easy to determine the values of $(d\Delta/dT)_p$ or $(d\alpha/dT)_p$ from the slopes of $\Delta \sim T$ or $\alpha \sim T$ isobars, and hence $(dV/dT)_p$ is obtained readily by substituting these values into the following equations:

$$\left(\frac{T}{V}\right)\left(\frac{dV}{dT}\right)_p = \frac{\frac{PV}{RT} - \left(\frac{T}{V}\right)\left(\frac{d\Delta}{dT}\right)_p}{1 + 2\frac{\Delta}{V}}, \tag{3}$$

$$\left(\frac{T}{V}\right)\left(\frac{dV}{dT}\right)_p = \frac{RT}{PV} - \frac{T}{V}\left(\frac{d\alpha}{dT}\right)_p. \tag{4}$$

The two values of $(dV/dT)_p$ at the same conditions which are obtained from Eqs. (3) and (4) respectively are plotted in $(T/V)(dV/dT)_p \sim P$, $(dV/dT)_p \sim T^{-1}$ and $PV(dV/dT)_p \sim T$ graphs and are corrected, by smoothing the curve of each isotherm or isobar, so that the values of $(dV/dT)_p$ at each condition thus obtained from these curves show reasonable coincidence among one another. Deming and Shupe have discussed that the $PV(dV/dT)_p \sim T$ isobars have turned out to be straight lines. In the present estimation, the isobars show the same behavior, except those near the critical condition and liquefying conditions and are very efficient for reasonable correction of $(dV/dT)_p$. The values of $(dV/dT)_p$ thus obtained are listed in Table 2 and $(dV/dT)_p \sim T$ isobars are shown in Fig. 3.

On the accuracy of $(dV/dT)_p$, Deming and Shupe have discussed "a 1 percent error in estimating the slope of Δ *vs.* T or an α *vs.* T isobar may mean only a few hundredths

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** Volume at 0°C, 1 atm: 22.2222 liters/mole
Thermal expansion coefficients at 1 atm: 0.003771 (at 0°C), 0.003738 (0° ~ 100°C)
Inter. Crit. Tables, 3, P. 3, 16

[8] R. Livingston, *Physico-Chemical Experiments*, P. 21, Macmillan Co., (1939)

Table 2 The thermal expansion coefficient of acetylene at constant pressure

$\left(\frac{dV}{dT}\right)_p \times 10^3$, (liters deg^{-1} mole^{-1})

P,atm / T, °C	10	20	30	40	50	60	70	80	90	100	110	120	130
0	10.9	7.96											
10	10.5	7.15	6.70										
20	10.1	6.53	5.73	6.29									
30	9.76	6.07	5.01	5.00	5.90								
40	9.46	5.67	4.56	4.25	4.53	5.92	3.70						
50	9.23	5.37	4.22	3.73	3.72	4.18	3.51	3.15	2.61	1.75	1.10	0.800	0.593
60	9.01	5.14	3.94	3.40	3.19	3.35	3.08	2.81	2.71	2.28	1.60	1.09	0.771
70	8.84	4.94	3.72	3.16	2.86	2.78	2.63	2.49	2.37	2.22	1.93	1.54	1.04
80	8.71	4.79	3.55	2.97	2.65	2.47	2.34	2.22	2.12	2.01	1.88	1.65	1.40
90	8.61	4.68	3.42	2.82	2.49	2.29	2.14	2.02	1.91	1.81	1.71	1.60	1.46
100	8.53	4.59	3.31	2.72	2.37	2.15	2.00	1.87	1.76	1.67	1.56	1.47	1.39
125	8.40	4.41	3.14	2.52	2.16	1.92	1.74	1.60	1.47	1.37	1.29	1.21	1.14
150	8.34	4.34	3.04	2.40	2.04	1.78	1.59	1.45	1.33	1.23	1.14	1.07	1.01
175	8.32	4.29	2.98	2.33	1.95	1.68	1.48	1.34	1.22	1.13	1.06	0.989	0.938
200	8.30	4.26	2.94	2.28	1.89	1.61	1.41	1.27	1.17	1.07	1.01	0.947	0.886
225	8.27	4.24	2.92	2.26	1.85	1.56	1.37	1.23	1.13	1.04	0.968	0.909	0.857
250	8.26	4.22	2.91	2.22	1.83	1.54	1.34	1.21	1.10	1.02	0.946	0.885	0.832

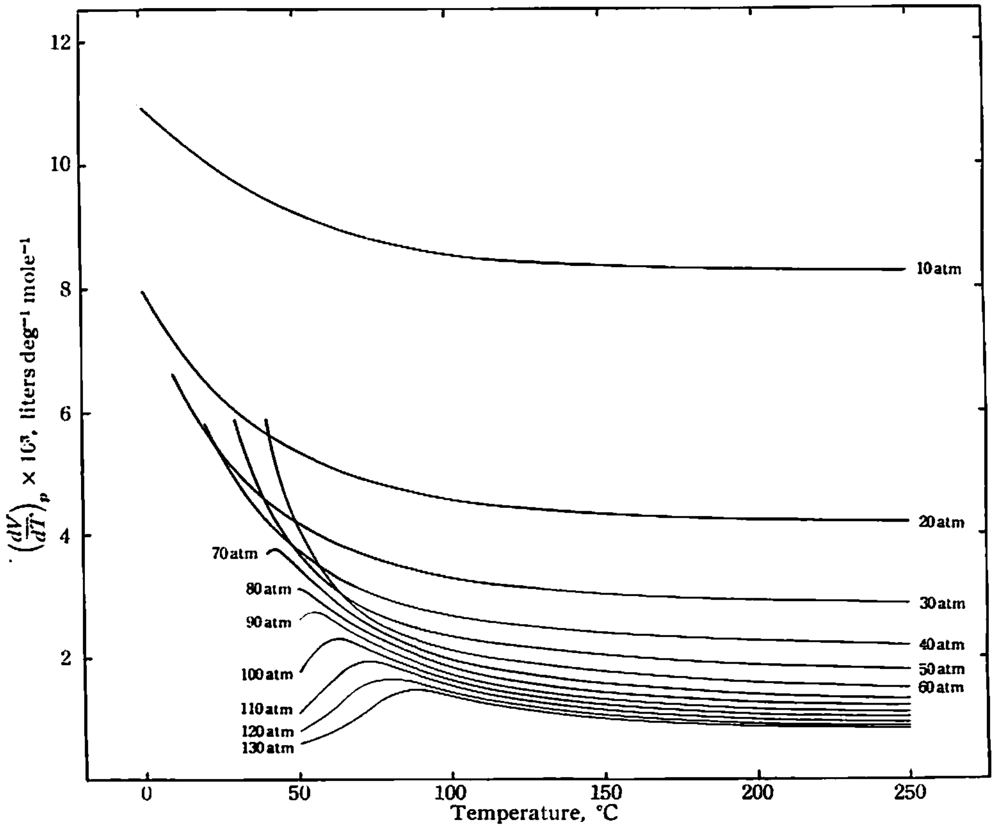

Fig. 3 The thermal expansion coefficient of acetylene at constant pressure

percent error in $(dV/dT)_p$, since by Eqs. (3) and (4) the slopes $(d\Delta/dT)_p$ and $(d\alpha/dT)_p$ enter as correction terms to the slope that the v *vs.* T isobar would have if the gas were perfect." However, all of their estimation are under such the conditions that T_r is more than 1.66 for N_2, CO and H_2, and on the other hand, in such the conditions that T_r is 0.88 ~ 1.69, as in the case of the present estimation, the deviations from the ideal gas law, that is the values of Δ and α, become larger and, especially near the critical point, their absolute values become as large as that of the volume, and consequently, it would be considered that the error of $(d\Delta/dT)_p$ or $(d\alpha/dT)_p$ would be more effective to the error of $(dV/dT)_p$ than that reported by Deming and Shupe. Considering from the differences between the two values of $(dV/dT)_p$ under the same conditions which are estimated from $(d\Delta/dT)_p$ and $(d\alpha/dT)_p$, the values listed in Table 2 are taken to have the following errors.

		Maximum (%)	Average (%)
100 ~ 250°C		0.8	0.6
0 ~ 100°C	below P_c	2.8	0.9
〃	above P_c	5.6	2.0

Heat Capacity at Constant Pressure

The next thermodynamic equation is used for estimating the heat capacity at constant pressure C_p,

$$\left(\frac{dC_p}{dP}\right)_T = -T\left(\frac{d^2V}{dT^2}\right)_p . \qquad (5)$$

By integration with P, the following equation is obtained,

$$C_p = C_p^\circ + \Delta C_p = C_p^\circ + \int_0^p -T\left(\frac{d^2V}{dT^2}\right)_p dP, \qquad (6)$$

where C_p° is the value of C_p under the standard state at each temperature, and in the present estimation, 1 atm is taken as the standard state, and the value of C_p° for acetylene at each temperature is obtained by the following equation which is calculated by Spencer[9] from the spectroscopic measurements on acetylene, that is,

$$C_p^\circ = 12.184 + 3.879 \times 10^{-3} T - 2.581 \times 10^{5} T^{-2} \text{ cal deg}^{-1} \text{ mole}^{-1}. \qquad (7)$$

The equation is reported to be applicable for the temperature between 298.16 and 1500°K within the error maximum 1.24 and average 0.59%***. $(d^2V/dT^2)_p$ is evaluated from the slope of the $(dV/dT)_p \sim T$ isobar and ΔC_p is obtained by graphical integration of $T(d^2V/dT^2)_p \sim P$ isotherm from 1 atm to the desired pressure. The results of the estimation of ΔC_p and C_p for acetylene are listed in Table 3 and $C_p \sim P$ isotherms are shown in Fig. 4.

It is difficult to mention the accuracy of $(d^2V/dT^2)_p$ as a whole, and however, its

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*** For the evaluation of C_p° values of 0°, 10°, and 20°C, the Eq. (7) has been used, because more adequate method of evaluation has not been obtained otherwise.

9) H. M. Spencer, *Ind. Eng. Chem.*, 40, 2152 (1948)

Table 3 The heat capacity of acetylene at constant pressure

$$\Delta C_p = \int_1^p -T\left(\frac{d^2V}{dT^2}\right)_p dP, \text{ (cal deg}^{-1}\text{ mole}^{-1}\text{)}$$

T, °C	P, atm	1	10	20	30	40	50	60	70	80	90	100	110	120	130
0	ΔC_p		3.8	11											
	C_p	9.78	13.6	21											
10	ΔC_p		3.3	8.1	14										
	C_p	10.06	13.4	18.1	24										
20	ΔC_p		2.8	6.4	11	20									
	C_p	10.32	13.1	16.7	21	30									
30	ΔC_p		2.3	5.2	8.9	14	24								
	C_p	10.55	12.9	15.8	19.4	24	35								
40	ΔC_p		1.9	4.2	7.0	11	17	30							
	C_p	10.77	12.7	15.0	17.7	21	27	41							
50	ΔC_p		1.6	3.3	5.5	8.2	12	19							
	C_p	10.97	12.5	14.2	16.5	19.1	23	29							
60	ΔC_p		1.3	2.7	4.5	6.4	9.0	13	19	24	27	27	25	23	20
	C_p	11.15	12.4	13.8	15.6	17.5	20.1	24	30	35	38	38	37	34	31
70	ΔC_p		1.0	2.2	3.6	5.2	7.0	9.6	13	16	20	22	22	21	19
	C_p	11.32	12.4	13.5	14.9	16.5	18.3	20.9	24	28	31	33	33	32	30
80	ΔC_p		0.86	1.8	2.9	4.3	5.7	7.6	9.7	12	14	16	18	19	17
	C_p	11.48	12.34	13.3	14.4	15.8	17.2	19.1	21.2	23	26	28	29	30	29
90	ΔC_p		0.68	1.5	2.5	3.5	4.7	6.1	7.6	9.2	11	12	14	15	16
	C_p	11.64	12.31	13.1	14.1	15.2	16.4	17.7	19.2	20.8	23	24	26	27	27
100	ΔC_p		0.54	1.2	2.0	2.8	3.8	4.9	6.1	7.3	8.6	10.0	11	13	14
	C_p	11.78	12.32	13.0	13.8	14.6	15.6	16.7	17.8	19.1	20.4	21.8	23	24	25
125	ΔC_p		0.33	0.74	1.2	1.8	2.4	3.0	3.7	4.5	5.2	6.0	6.9	7.6	8.4
	C_p	12.10	12.43	12.84	13.3	13.9	14.5	15.1	15.8	16.6	17.3	18.1	19.0	19.7	20.5
150	ΔC_p		0.22	0.50	0.81	1.1	1.5	1.9	2.3	2.8	3.3	3.8	4.3	4.8	5.3
	C_p	12.38	12.61	12.88	13.19	13.5	13.9	14.3	14.7	15.2	15.7	16.2	16.7	17.2	17.6
175	ΔC_p		0.13	0.28	0.46	0.67	0.89	1.1	1.4	1.7	2.0	2.3	2.7	3.0	3.3
	C_p	12.64	12.76	12.92	13.10	13.30	13.53	13.8	14.1	14.4	14.7	15.0	15.3	15.7	16.0
200	ΔC_p		0.09	0.20	0.32	0.47	0.62	0.79	0.96	1.1	1.4	1.6	1.8	2.0	2.2
	C_p	12.87	12.95	13.06	13.19	13.33	13.48	13.65	13.83	14.0	14.2	14.4	14.6	14.8	15.0
225	ΔC_p		0.07	0.15	0.25	0.36	0.48	0.61	0.76	0.91	1.1	1.2	1.4	1.6	1.7
	C_p	13.08	13.14	13.23	13.32	13.43	13.55	13.69	13.83	13.99	14.2	14.3	14.5	14.6	14.8
250	ΔC_p		0.06	0.13	0.21	0.31	0.41	0.52	0.65	0.78	0.91	1.1	1.2	1.3	1.5
	C_p	13.27	13.33	13.40	13.84	13.58	13.68	13.79	13.92	14.05	14.18	14.3	14.5	14.6	14.7

several examples which are calculated from the errors of $(dV/dT)_p$ and of the slopes of $(dV/dT)_p \sim T$ isotherms are shown below.

175°C, 90 atm: 0.82% 60°C, 110 atm: 7.5%
90°C, 40 atm: 0.85% 20°C, 30 atm: 1.0%

The error involved in the graphical integration is estimated to be about ±0.2% and considering these errors, the values of ΔC_p in Table 3 are taken to have the probable errors of 0.8 ~ 8.0%, and the ranges of the errors are shown by the dotted lines on both sides of each isotherm in Fig. 4.

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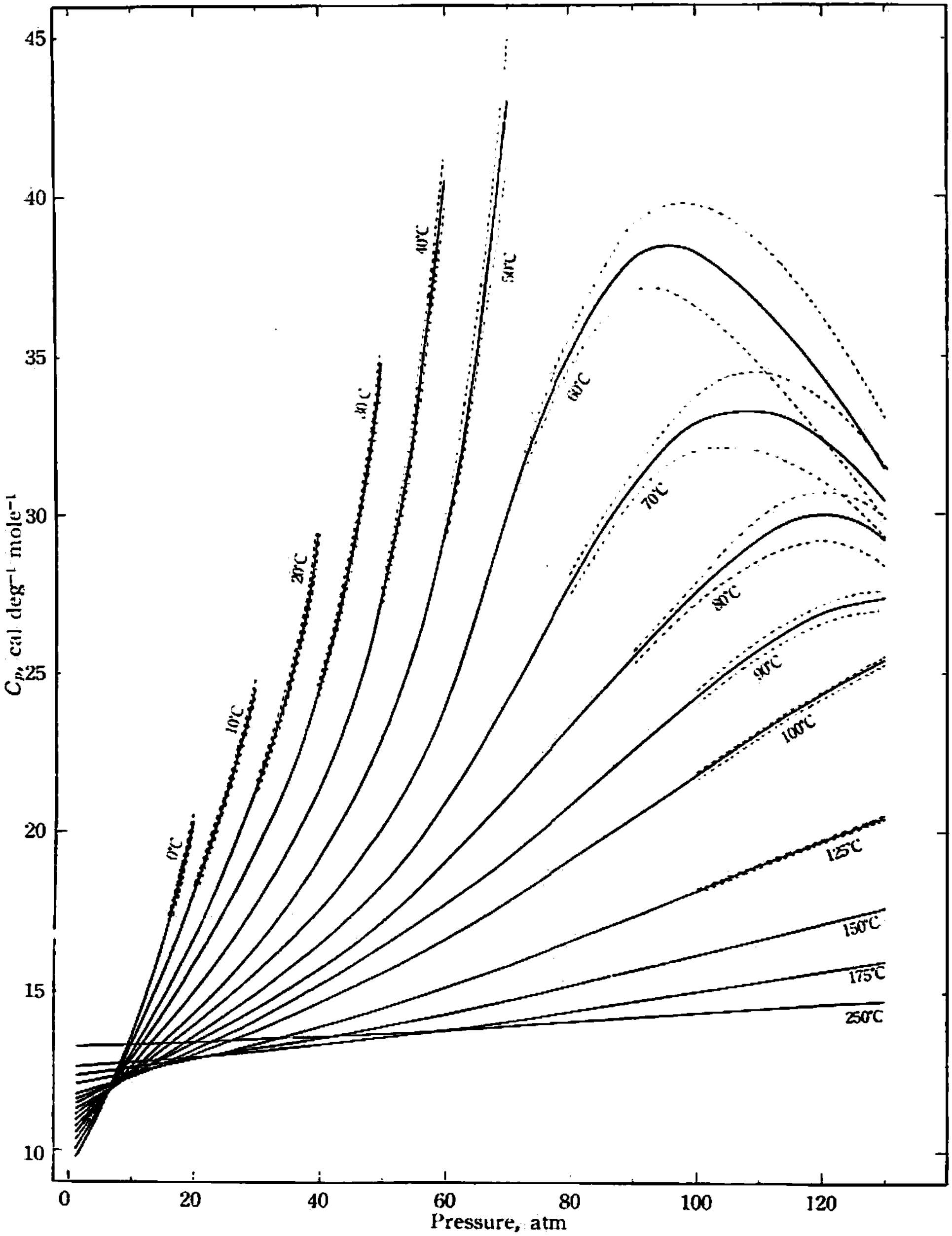

Fig. 4 The heat capacity of acetylene at constant pressure

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