pVT relation of CO_2 and the phenomena of critical points

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I. INTRODUCTION

Ideal gas law can only describe gases at relatively low pressure and a high temperature. It completely neglects the interaction between gas molecules as well as the volume of them, thus it is unable to describe nor predict condensed states. Van der Waals equation, however, takes the two neglected factors into consideration, which succeeds in predicting the liquid state.

The Van der Waals eqaution can be deduced starting from a few approximations from thermostatistical models. Sutherland potential function gives

$$u(r) = \begin{cases} -\epsilon(\frac{r_0}{r})^6 & r > r_0 \\ \infty & r \leqslant r_0 \end{cases} \tag{1}$$

Define f as

$$f = e^{-\beta u(r)} - 1 \tag{2}$$

then virial coefficient of second grade B_2 can be written as

$$B_2 = -\frac{N_A}{2} \int f d\vec{r} \tag{3}$$

thus

$$B_2 = 2\pi N_A \left[\int_0^{r_0} r^2 \, dr - \int_{r_0}^{\infty} f r^2 dr \right] \tag{4}$$

which can be approximated as

$$B_2 \sim 2\pi N_A \left[\frac{r_0^2}{3} - \frac{r_0^3 \beta u_0}{3} \right] \tag{5}$$

Defining

$$b = \frac{2\pi}{3} N_A r_0^3, a = \frac{2\pi}{3} N_A^2 u_0 r_0^3 \tag{6}$$

B_2 can be rewritten as

$$B_2 = b - \frac{a}{N_A kT} \tag{7}$$

thus

$$\begin{aligned} pV &= NkT \left(1 + \frac{nB_2}{V}\right) \\ &= NkT \left(1 + \frac{nb}{V} - \frac{na}{N_A V kT}\right) \\ &= NkT \left(1 + \frac{nb}{V}\right) - \frac{n^2 a}{V} \end{aligned}$$

TABLE I. The fitting parameters of the Van der Waals equation

$T/°C$	$10^4 a$	b	c	R^2
20.0	-0.0304197	-0.142756	0.944498	0.985071
23.0	-0.035569	-0.116091	0.831901	0.992765
25.0	-0.0126799	-0.0825918	0.74025	0.991335
27.0	-0.008464	-0.0721021	0.705178	0.992875
29.0	-0.00179595	-0.0692964	0.718065	0.994144
34.2	0.00952114	-0.0599663	0.700013	0.997943
40.0	0.0136454	-0.05091	0.677438	0.998828
45.0	0.100063	-0.0284707	0.59214	0.999935

An approximation that $\frac{nb}{V}$ is comparatively small leads to

$$pV = \frac{NkT}{1 - \frac{nb}{V}} - \frac{n^2 a}{V} \tag{8}$$

which is a equivalent form of Van der Waals equation.

At a relatively low temperature $\frac{\partial p}{\partial V} > 0$ no longer satisfies, and there exists p_c, V_c, T_c such that

$$\begin{cases} \left(\frac{\partial p}{\partial V}\right)\Big|_{V=V_c} = 0 \\ \left(\frac{\partial^2 p}{\partial V^2}\right)\Big|_{V=V_c} = 0 \end{cases} \tag{9}$$

which leads to the solution

$$V_c = 3nb, T_c = \frac{8}{27bR}, p_c = \frac{4a}{27b^2} \tag{10}$$

which is called critical point. Around this point several phenomena can be observed.

II. METHODS AND PROCEDURES

pVT measurement apparatus - which consists of pump pressure gauge, a thermostat and a graduated tube containing CO_2 - is utilized in this experiment. Pressure is accumulated gradually until it reaches 10 MPa, during the process of which several points are chosen and the height of mercury in the tube is measured. The volume per area of cross section of the tube is calculated w.r.t. the volume per area of cross section of CO_2 liquid at 9.8 MPa and 20 °C.

TABLE II. The raw data of the experiment, where the upper row in each box represents the pressure of the system in MPa, while the lower row the volume per kilogram of $CO_2 (m^3/kg)$.

20.0 °C

2.42	3.05	4.00	5.05	5.55	5.67	5.77	6.45	6.72	7.95	9.80
0.0183	0.0142	0.00981	0.00676	0.00547	0.00460	0.00325	0.00166	0.00128	0.00121	0.00117

23.0 °C

2.27	2.98	4.05	5.11	6.05	6.20	7.44	8.45	9.77
0.0200	0.0149	0.00983	0.00687	0.00442	0.00242	0.00136	0.00128	0.00121

25.0 °C

2.50	3.28	4.00	4.96	6.02	6.40	6.80	7.40	8.07	9.73
0.0182	0.0133	0.0103	0.00740	0.00498	0.00317	0.00143	0.00136	0.00133	0.00125

27.0 °C

2.29	3.08	4.08	4.98	6.04	6.48	6.62	6.87	7.68	8.48	9.85
0.0203	0.0145	0.0101	0.00759	0.00517	0.00408	0.00321	0.00170	0.00140	0.00132	0.00128

29.0 °C

2.17	3.10	3.99	5.00	6.10	6.88	7.10	7.68	8.68	9.75
0.0219	0.0146	0.0121	0.00766	0.00532	0.00362	0.00200	0.00143	0.00132	0.00132

34.2 °C

2.05	3.01	3.98	4.95	5.95	6.90	7.10	7.20	7.30	7.40	7.50	7.60	7.75	7.78	8.00	8.43	9.70
0.0235	0.0155	0.0110	0.00819	0.00604	0.00442	0.00408	0.00393	0.00377	0.00351	0.00332	0.00302	0.00279	0.00257	0.00181	0.00159	0.00143

40.0 °C

2.40	3.04	4.00	5.00	5.95	6.95	7.42	7.93	8.45	9.18	9.78
0.0204	0.0159	0.0114	0.00849	0.00668	0.00494	0.00430	0.00279	0.00279	0.00189	0.00159

45.0 °C

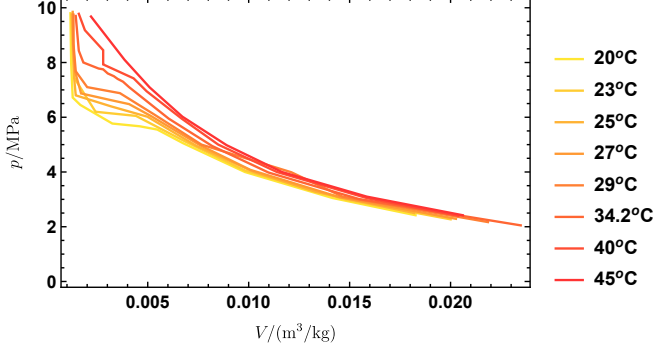| 2.42	3.10	4.00	4.98	6.02	7.09	8.10	9.68
0.0206	0.0159	0.0116	0.00891	0.00672	0.00510	0.00385	0.00219

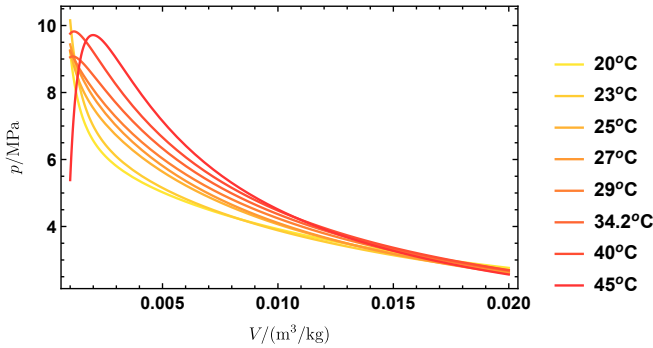FIG. 1. $p - V$ line plots of CO_2 at different temperature

FIG. 2. $p - V$ line plots of CO_2 fitted by Van der Waals equation

III. RESULTS AND ANALYSIS

The $p - V$ line plots are given in Fig. 1, with its fits by Van der Waals equation, namely

$$p = \frac{c}{V - b} - \frac{a}{V^2} \quad (11)$$

where a, b, c are constants, and V is defined as volume per kilogram of CO_2. The fitting parameters are given in Table I. It should be noted that only points where the CO_2 only appears as one phase are considered in the fitting. Result shows that Van der Waals equation fitting fails to give a positive b, which might be attributed to the fluctuations of data due to deviation from equilibrium states that greatly affects the non linear fitting process, as well as the deficiency of Van der Waals equation when describing the CO_2 liquid.

The critical point is suggested as

$$T_c = 307.3 \, \text{K}, V_c = 0.00377 \, \text{m}^3/\text{kg}, \, p_c = 7.30 \, \text{MPa} \quad (12)$$

while the theoretical critical point of CO_2 is given as

$$T_c = 304.2 \, \text{K}, \, p_c = 7.38 \, \text{MPa} \quad (13)$$

Factors are manifold. Impurity of the CO_2 as well as the deviation from equilibrium states can account for the error, while the non-uniform temperature distribution of the thermostats mainly contributes to the error in measurement of the temperature of the critical point, as is described in older reports. What makes the situation worse is that only a plastic tube with no coating materials is connected between the thermostat and the measuring device, deteriorating the circulation of the water and strengthening the heat loss. The rigidness of the tube containing CO_2 should also be doubted, which may affect the measurement of volumes and a non linear effect on the $p - V$ curve.

A sudden phase transition accompanied with light scattering effect is observed, which should be attributed to very small amount of heat required for evaporation, while the fast transition leads to small radius of the liquid drops formed. Rayleigh successfully predicts the scattering light through these 'particles' by regarding them as a resonance of the electromagnetic field in the particles and the light, emitting light in all directions at the same wavelength. The identical phisical properties of the liquid phase and the gas phase leads to small deviations of reflection rate between two phases, resulting in the blurred phase surface.

IV. CONCLUSIONS

The pVT curves of CO_2 around its critical point is plotted. Errors in the prediction of critical points are mainly attributed to many factors, including the non uniform distribution of temperature, deviation from equilibrium states and the impurity of CO_2. Sudden phase transition is an identical phenomenon for gases near their critical points.