SOME PROPERTIES OF A VAN DER WAALS GAS

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ABSTRACT

The thermodynamic functions of an ideal substance represented by van der Waals equation are obtained with the help of the condition that these functions reduce to those of a perfect gas in the limiting case of vanishing pressure. The volumes of the liquid state and gas state in coexistence as determined by Maxwell's rule of equal areas are expressed in a parametric form. The nature of the dependence of the constants a and b on the chemical composition of the gas is briefly considered.

1. *The thermodynamic functions*

The consequences of van der Waals equation have been very fully investigated[1], but there still remain some points which may be of interest to discuss here. The equation of state will be taken in a slightly more general form:

$$\left(p+\frac{a}{T^n V^2}\right)(V-b)=NRT, \tag{1}$$

which reduces to the original van der Waals equation when $n=0$ and to Berthelot's equation when $n=1$. N is the number of moles, and the constants a and b refer to the whole gas.

In order to obtain the thermodynamic functions, the simplest way is to find the free energy of Helmholtz first, because the free energy is a characteristic function for the independent variables T and V so that all other thermodynamic functions can be deduced from it. In the equation

$$p=-\frac{\partial F}{\partial V}$$

we substitute the expression of p given by (1) and integrate. The result is

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[1] See, for example, *Handbuch der Physik* X (1926), pp. 126-222.

$$F = -NRT\ln(V-b) - \frac{a}{T^nV} + C,$$

where C is a constant of integration depending on the temperature. To determine C we utilize the fact that when the volume becomes very large the gas approaches a perfect gas. Hence

$$F = -NRT\ln(V-b) - \frac{a}{T^nV} - T\int\frac{dT}{T^2}\int C_v^o\,dT - TS_0 + U_0, \qquad (2)$$

where C_v^o is the heat capacity (at constant volume) of the gas in the limiting case of vanishing pressure or infinite volume, and U_0 and S_0 are the energy and entropy constants respectively. C_v^o depends only on the temperature.

The other thermodynamic functions are:

$$U = -T^2\frac{\partial}{\partial T}\frac{F}{T} = -\frac{(n+1)a}{T^nV} + \int C_v^o\,dT + U_0, \qquad (3)$$

$$S = -\frac{\partial F}{\partial T} = NR\ln(V-b) - \frac{na}{T^{n+1}V} + \int\frac{C_v^o}{T}\,dT + S_0. \qquad (4)$$

$$H = U + pV = \frac{NRTV}{V-b} - \frac{(n+2)a}{T^nV} + \int C_v^o\,dT + U_0. \qquad (5)$$

$$G = F + pV = -NRT\ln(V-b) + \frac{NRTV}{V-b} - \frac{2a}{T^nV}$$

$$- T\int\frac{dT}{T^2}\int C_v^o\,dT - TS_0 + U_0. \qquad (6)$$

The heat capacity at constant volume is

$$C_v = \frac{\partial U}{\partial T} = C_v^o + \frac{n(n+1)a}{T^{n+1}V}. \qquad (7)$$

This is independent of volume when $n=0$. Using the well-known thermodynamic relation for $C_p - C_v$, we find

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2. Similar results have been obtained by J. J. van Laar and R. Lorenz (*Zeit. anorg. u. allg. Chem.* 145 (1925), 239) by using a more complicated method. Professor Tzu-ching Huang of the Department of Chemistry informed me of this work after my paper was submitted to him, and I wish to express my gratitude to him.

$$C_p - C_v = \frac{[NRT^{n+1}V^3 + na(V-b)^2]^2}{T^{n+1}[NRT^{n+1}V^3 - 2a(V-b)^2]} \cdot \tag{8}$$

The above method of obtaining the thermodynamic functions is applicable to any other equation of state of gases. For example, if the equation of state is expressed as a power series of $1/V$ in the form

$$pV = NRT + \frac{B}{V} + \frac{C}{V^2} + \cdots, \tag{9}$$

we have

$$F = -NRT \ln V + \frac{B}{V} + \frac{C}{2V^2} + \cdots$$
$$- T \int \frac{dT}{T^2} \int C_v^0 \, dT - TS_0 + U_0 \, . \tag{10}$$

On the other hand, if the equation of state is expressed as a power series of p:

$$pV = NRT + Bp + Cp^2 + \cdots, \tag{11}$$

then it is more convenient to determine the Gibbs function first, and the result is

$$G = NRT \ln p + Bp + \tfrac{1}{2} Cp^2 + \cdots$$
$$T \int \frac{dT}{T^2} \int C_p^0 \, dT - TS_0 + H_0 \, . \tag{12}$$

§2. *Condensation*

The pressure of the saturated vapour is determined by the well-known rule of equal areas (Maxwell). This rule can be deduced from the condition of mini-

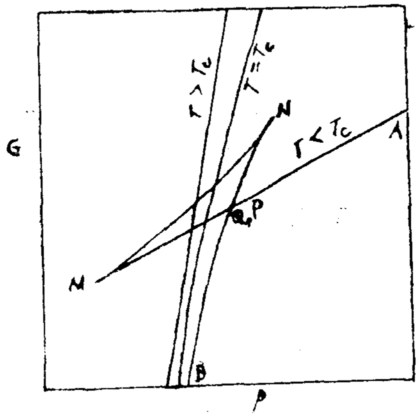

Fig. 1 — Isothermals of Gibbs function.

mum F at constant T and V. It can also be deduced from the condition of minimum G at constant T and p. The graph of G is shown in fig. 1. It is seen that when the temperature is below the critical temperature (T_c), the curve has a double point (P, Q). The branches AP, BQ have lower values of G than the branches PM, MN, NQ. The part AP represents the liquid state and the part BQ represents the gas state. The pressure p_s of the saturated vapour is the pressure at P or Q. This pressure is determined by the equation

$$G_P = G_Q. \tag{13}$$

or

$$F_P + p_s V_l = F_Q + p_s V_g.$$

where V_l, V_g are the volumes of liquid and gas respectively. This can be written as

$$p_s(V_g - V_l) = \int_{V_l}^{V_g} p\,dv, \tag{13'}$$

which is the rule of equal areas.

Substituting (6) into (13), we obtain

$$-NRT\ln(V_l - b) + \frac{NRTV_l}{V_l - b} - \frac{2a}{T^n V_l}$$
$$= -NRT\ln(V_g - b) + \frac{NRTV_g}{V_g - b} - \frac{2a}{T^n V_g}. \tag{14}$$

From (1) we have

$$p_s = \frac{NRT}{V_l - b} - \frac{a}{T^n V_l^2} = \frac{NRT}{V_g - b} - \frac{a}{T^n V_g^2}. \tag{15}$$

The equations (14) and (15) determine the three quantities p_s, V_l, V_g as functions of temperature.

Let

$$V_l - b = \alpha(V_g - b). \tag{16}$$

We shall use α as a parameter and express other quantities in terms of it. Eliminating T from (14) and (15) and using (16); we obtain

$$\frac{V_g}{b} = \frac{1-\alpha}{\alpha} \cdot \frac{\alpha - \alpha \ln \alpha - 1}{(1+\alpha)\ln \alpha + 2(1-\alpha)}, \tag{17}$$

$$\frac{V_l}{b} = \frac{(1-\alpha)(\ln \alpha + 1 - \alpha)}{(1+\alpha)\ln \alpha + 2(1-\alpha)}, \tag{18}$$

$$T^{n+1} = \frac{a}{NR} \frac{(V_g+V_l)(V_g-b)(V_l-b)}{V_g^2 V_l^2}. \tag{19}$$

When α increases from 0 to 1, $NRT^{n+1}\, b/a$ increases from 0 to 8/27, V_g decreases from ∞ to $3b$, V_l increases from b to $3b$. The critical point corresponds to $\alpha = 1$.

3. *The heterogeneous region*

When V lies between V_l and V_g, the substance is a heterogeneous mixture of gas and liquid. If x is the fraction of gas, then

$$V = x V_g + (1-x) V_l. \tag{20}$$

The free energy is also of this form:

$$F = x F_g + (1-x) F_l, \tag{21}$$

from which one can see that all other thermodynamic functions are of the same form.

From (7) we obtain

$$C_{vl} - C_{vg} = \frac{n(n+1)a}{T^{n+1}} \left(\frac{1}{V_l} - \frac{1}{V_g} \right). \tag{22}$$

The difference between C_{pl} and C_{pg} can be obtained from (8). The expression is not written down on account of its complexity. It is seen from (22) that $C_{vl} > C_{vg}$. This is in qualitative agreement with observed facts.

In fig. 2 are shown isothermals of $(C_p - C_v)/NR$. Only the case $n=0$ is shown. The curves in the case $n>0$ are similar. For $T > T_c$ the curve has a maximum at $V = V_c$. At $T = T_c$ this maximum becomes infinite. For $T < T_c$ the curve becomes infinite at V_M and V_N, which are the volumes corresponding respectively to a minimum and a maximum in the $p-V$ graph.

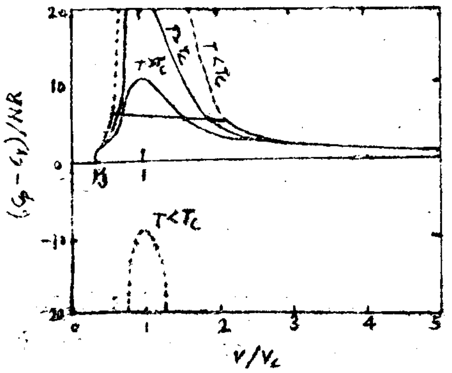

Fig. 2—Isothermals of $(C_p - C_v)/NR$ in the case of $n=0$.

Between V_M and V_N the value of $C_p - C_v$ becomes negative. But the volumes V_M and V_N lie between V_l and V_g, and the part of the curve lying in this region should be replaced by a straight line.

The latent heat of evaporation is obtained from (5):

$$L = H_g - H_l = NRT(V_g - V_l)\left\{\frac{(n+2)a}{NRT^{n+1}V_gV_l} - \frac{b}{(V_g-b)(V_l-b)}\right\}. \qquad (23)$$

When the temperature increases from 0 to the critical temperature the quantity L/NRT decreases from ∞ to 0.

It can be verified by a somewhat complicated calculation that Clapeyron's equation holds:

$$\frac{dp_s}{dT} = \frac{L}{T(V_g - V_l)}.$$

With the help of the expression (23) for the latent heat the specific heat of the saturated vapour can be calculated.

4. *The Joule-Thomson effect*

For the Joule-Thomson effect we have

$$\left(\frac{\partial H}{\partial p}\right)_T = -C_p\left(\frac{\partial T}{\partial p}\right)_H = \frac{V[NRT^{n+1}V^2b - (n+2)a(V-b)^2]}{NRT^{n+1}V^3 - 2a(V-b)^2} \qquad (24)$$

The denominator is proportional to the bulk modulus of elasticity and is always positive outside the heterogeneous region. The sign of the Joule-Thomson coefficient $(\partial T/\partial p)_H$ is therefore solely determined by the numerator. There is a cooling effect when

$$NRT^{n+1}b < a(n+2)(1-b/V)^2,$$

and a heating effect in the opposite case. The inversion temperature at which the Joule-Thomson coefficient vanishes is given by

$$NRT^{n+1}b = a(n+2)(1-b/V)^2. \tag{25}$$

This equation shows that the inversion temperature is a function of the volume. Solving for V from (25) and substituting into (1), we obtain the dependence of the inversion temperature on pressure:

$$p = \frac{NRT}{(n+2)b}\left(\sqrt{\frac{(n+2)a}{NRT^{n+1}b}} - 1\right)\left(n + 3 - \sqrt{\frac{(n+2)a}{NRT^{n+1}b}}\right). \tag{26}$$

When p is greater than the value given by this equation, the Joule-Thomson coefficient is negative and there is a heating effect. When p is less than this value, the Joule-Thomson coefficient is positive and there is a cooling effect.

In fig. 3 are plotted the curves of inversion temperatures. The experimental data for nitrogen[3] are given as circles for comparison.

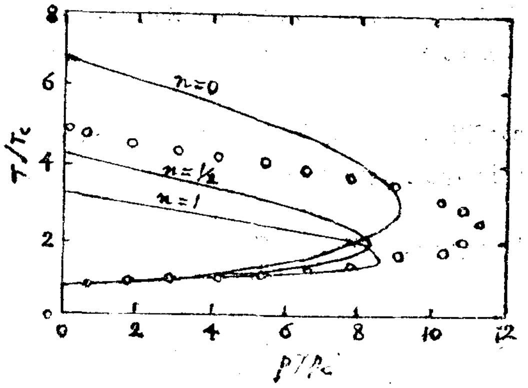

Fig. 3 – Curves of inversion temperatures in Joule-Thomson effect

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[3] J. R. Roebuck and H. Osterberg, *Phys. Rev.* 48 (1935), 450.

5. *Mixture of van der Waals gases*

Suppose that the gas consists of k kinds of molecules with N_i moles of the kind i. If we assume van der Waals equation (1) to apply to the mixture we must assume

$$N = \sum_{i=1}^{k} N_i , \tag{27}$$

and assume a and b to be functions of N_i. The simplest assumptions concerning a and b consistent with the condition of homogeneity are (i.e., b must be a homogeneous function of degree one in the N's in order that b may increase proportionately to V when the amount of the gas is increased without changing its other properties):

$$a = \tfrac{1}{2}\sum_{i,j} a_{ij} N_i N_j , \qquad (a_{ij} = a_{ji}), \qquad b = \sum_{i} b_i N_i , \tag{28}$$

where a_{ij} and b_i are constants. The earlier assumption[4] on b is also a quadratic dependence on the N's, but such an assumption has neither theoretical nor experimental foundation. From recent investigations of statistical mechanics it appears that a linear dependence of b on the N's is more reasonable.

The quantity b_i may be naively interpreted as four times the aggregate volume of ono mole of the gas molecules of kind i. The quantity a_{ij} may be interpreted as the constant of cohesive force between a molecule of kind i and one of kind j.

Using the condition that the free energy expression reduces to that of a perfect gas-mixture in the limiting case of vanishing pressure, we obtain

$$F = \sum_{i} N_i RT \ln \frac{N_i}{V-b} - \frac{a}{T^n V} + \sum_{i} N_i \left\{ -T \int \frac{dT}{T^2} \int C_{vi}^{0}\, dT - T s_{io} + u_{io} \right\} . \tag{29}$$

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[4] A linear dependence of b on the N's was also assumed by van Laar and Lorenz (*loc. cit.* 2). Cf. a paper by J. A. Beattie and S. Ikehara, *Proc. Amer Acad. Arts and Sci.* *64* (1930), 127; especially p. 131.

where c_{pi}^{0} are the molar heat capacities of the various components in the limiting case of vanishing pressure, and u_{io} and s_{io} are the respective energy and entropy constants.

From (29) all other thermodynamic functions can be deduced in the usual way. In particular, the chemical potential of the component i is

$$\mu_i = \frac{\partial F}{\partial N_i} = \mu_i^0(T) + RT \ln p_i^*, \tag{30}$$

with

$$\mu_i^0(T) = -T \int \frac{dT}{T^2} \int (C_{pi}^0 + R)\,dT - T s_{io} + u_{io} \tag{31}$$

and

$$RT \ln p_i^* = RT \ln \frac{N_i RT}{V-b} + \frac{NRTb_i}{V-b} - \frac{1}{2nV} \sum_j a_{ij} N_j. \tag{32}$$

The quantity p_i^* is called the "partial fugacity" of the component i by G. N. Lewis. As $V \to \infty$, we have $p_i^* \sim N_i RT/V$, which is the partial pressure of the component i.