GIBBS THERMODYNAMICAL MODEL FOR A SUB-
STANCE FOLLOWING VAN DER WAALS'
EQUATION.

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VAN DER WAALS' equation is commonly written

$$(1) \quad (p + a/v^2)(v-b) = RT.$$

For the purposes of a general discussion it is often convenient to suppress the three constants a , b , R , by taking the critical pressure volume and temperature as the units of pressure, volume, and temperature respectively. If these be called p_c , v_c , T_c , and the so-called *reduced* pressure, volume, and temperature be indicated by

$$\pi = \frac{p}{p_c}, \quad \varphi = \frac{v}{v_c}, \quad \vartheta = \frac{T}{T_c}.$$

It can be shown that the equation will reduce to the form

$$(2) \quad \left(\pi + \frac{3}{\varphi^2} \right) (3\varphi - 1) = 8\vartheta,$$

which *appears* to have no empirical constants.

The form of the isothermals, with whose general properties we are familiar, is shown in Fig. 1. In this figure we notice certain peculiarities. These we will discuss a little later.

In connection with questions raised in a previous article¹ it seemed to me desirable to find the form of a Gibbs' Thermodynamical Model for a substance whose properties in two states were represented by a comparatively simple analytical expression. A substance following van der Waals' equation is as much an ideal substance as is a perfect gas, yet it exhibits many properties common to actual substances. For a substance following equation (1) the first law of Thermodynamics

¹ PHYS. REV., 10, p. 228, 1900.

Fig. 1.

$$dQ = dU + p dv.$$

becomes

$$(3) \quad dQ = C_v dT + (p + a/v^2) dv$$

from which it readily appears that

$$dU = C_v dT + a/v^2 dv$$

and if we regard C_v as a constant, an assumption entirely in harmony with, and even suggested by, those ideas of the Kinetic Theory which gives us the original equation, we have

$$(4) \quad U = \int_0^T C_v dT + \int_b^v \frac{a}{v^2} dv = C_v T + \frac{a}{b} - \frac{a}{v}.$$

The coördinates of the surface we wish are the energy, volume and

entropy. We may introduce the latter and eliminate T by comparing (3) with

$$dQ = TdS$$

from which we can deduce

$$(5) \quad S = C_v \log T + R \log (v - b) + \text{Const}$$

$$T = K' e^{\frac{S}{C_v}} (v - b)^{-\frac{R}{C_v}}$$

and substituting in (4),

$$(6) \quad U = K e^{\frac{S}{C_v}} (v - b)^{-\frac{R}{C_v}} + a/b - a/v$$

where

$$K = C_v K'.$$

R/C_v is a constant, equal, according to the Kinetic Theory, to two-thirds of the ratio of the kinetic energy of translation of the molecules to their total energy, or to $\frac{C_p}{C_v} - 1$ very nearly, that is, in ideal cases such as we are considering, to $2/3$, $2/5$, $2/6$, $2/7$, etc. This then is the equation of the model, and we see immediately that it satisfies the differential equations

$$T = \frac{\partial U}{\partial S} = K e^{\frac{S}{C_v}} (v - b)^{-\frac{R}{C_v}} / C_v = K' e^{\frac{S}{C_v}} (v - b)^{-\frac{R}{C_v}}$$

$$\begin{aligned} p = - \frac{\partial U}{\partial v} &= \frac{R}{C_v} K e^{\frac{S}{C_v}} (v - b)^{-1 - \frac{R}{C_v}} - \frac{a}{v^2} \\ &= \frac{RT}{v - b} - \frac{a}{v^2}. \end{aligned}$$

For a general discussion it is desirable to have the equation in terms of the reduced coördinates. At the critical state equation (5) becomes

$$S_c = C_v \log T_c + R \log (v_c - b) + \text{Const}$$

and hence

$$S - S_c = C_v \log \frac{T}{T_c} + R \log \frac{v - b}{v_c - b}$$

or remembering that

$$T/T_c = \vartheta, \quad b = v_c/3, \quad v/v_c = \varphi$$

$$(7) \quad S - S_e = C_v \log \vartheta + R \log \frac{3\varphi - 1}{2}$$

whence

$$(8) \quad \vartheta = e^{(S - S_e)/C_v} \left(\frac{3\varphi - 1}{2} \right)^{-R/C_v}$$

$$\text{Equation (4)} \quad U = C_v T + a/b - a/v$$

gives, substituting for T and v their values

$$\begin{aligned} T &= \vartheta T_e = \frac{8a}{27bR} \vartheta \\ v &= \varphi v_e = 3b\varphi \\ U &= \frac{8aC_v}{27bR} \vartheta + \frac{a}{b} - \frac{a}{3b\varphi} \\ &= \frac{a}{b} \left(\frac{8C_v}{27R} \vartheta + \frac{3\varphi - 1}{3\varphi} \right) \end{aligned}$$

and substituting the value of ϑ just found,

$$U = \frac{a}{b} \left[\frac{8C_v}{27R} e^{(S - S_e)/C_v} \left(\frac{3\varphi - 1}{2} \right)^{-R/C_v} + \frac{3\varphi - 1}{3\varphi} \right]$$

which contains no arbitrary constant except S_e , but does contain the factor a/b which depends upon the properties of the substance. At the critical state

$$U_e = \frac{a}{b} \left[\frac{8C_v}{27R} + \frac{2}{3} \right]$$

which enables us to express U entirely in terms of the properties of the critical state.

$$\frac{U}{U_e} = \frac{\frac{8}{27} \frac{C_v}{R} e^{\frac{S - S_e}{C_v}} \left(\frac{3\varphi - 1}{2} \right)^{-\frac{R}{C_v}} + \frac{3\varphi - 1}{3\varphi}}{\frac{8}{27} \frac{C_v}{R} + \frac{2}{3}}$$

or letting

$$\begin{aligned} \varphi &= x \\ (S - S_e)/C_v &= y \\ U/U_e &= z \end{aligned}$$

$$z = \frac{\frac{8}{27} \frac{C_v}{R} e^y \left(\frac{3x-1}{2} \right)^{-\frac{R}{C_v}} + \frac{3x-1}{3x}}{\frac{8}{27} \frac{C_v}{R} + \frac{2}{3}}.$$

The general properties of this equation are very much the same for the different values of the ratio $\frac{R}{C_v}$. For my computations I have selected the value $2/7$, suggested by the Kinetic Theory for such triatomic gases as H_2O and CO_2 . For these it becomes.

$$(9) \quad z = \frac{14}{23} e^y \left(\frac{3x-1}{2} \right)^{-\frac{2}{7}} + \frac{9}{46} \frac{3x-1}{x}.$$

The general form of the surface is shown by Fig. 2, sections by planes of constant entropy, $y = \text{const.}$

Fig. 2.

ISOTHERMALS.

Equation (7) becomes, dividing both members by C_v and substituting the new variables,

$$(10) \quad \begin{aligned} y &= \log \vartheta + \frac{R}{C_v} \log \frac{3x-1}{2} \\ &= \log \vartheta + \frac{2}{7} \log \frac{3x-1}{2}. \end{aligned}$$

These curves are shown in Fig. 3 for the same values of ϑ which were employed in Fig. 1.

Fig. 3.

ISOPIESTICS.

Similarly substituting in (2) the value of ϑ in (8), and changing the coördinates, we obtain as the equation of the isopiestic,

$$(11) \quad y = \log \left(\pi + \frac{3}{x^2} \right) + \frac{9}{7} \log \frac{3x-1}{2} - \log 4.$$

These curves also are shown in Fig. 3.

LINE OF INSTABILITY.

The unstable and explosive condition corresponding to certain states of a substance following van der Waals' equation is characterized by the fact that when the temperature is kept constant an increase of volume is accompanied by an increase of pressure, and vice versa, or analytically

$$\frac{\partial p}{\partial v} (T = \text{Const}) > 0.$$

The curve limiting this unstable region will then have the differential equation

$$\frac{\partial \pi}{\partial \varphi_{(2)}} = 0.$$

It is most convenient to obtain this directly from (2), writing

$$\begin{aligned}\pi &= \frac{8\vartheta}{3\varphi - 1} - \frac{3}{\varphi^2}, \\ \frac{\partial \pi}{\partial \varphi} &= -\frac{3 \cdot 8\vartheta}{(3\varphi - 1)^2} + \frac{6}{\varphi^3} = 0, \\ 4\vartheta &= \frac{(3\varphi - 1)^2}{\varphi^3}.\end{aligned}$$

Eliminating ϑ between this equation and (2) we have

$$(12) \quad \pi = \frac{2(3\varphi - 1)}{\varphi^3} - \frac{3}{\varphi^2},$$

the equation of the broken line in Fig. 1. Eliminating instead with (8), and making the same substitutions as before, we have

$$\begin{aligned}(13) \quad e^y &= \frac{1}{x^3} \left(\frac{3x - 1}{2} \right)^{\frac{16}{7}} \\ y &= \frac{16}{7} \log \frac{3x - 1}{2} - 3 \log x,\end{aligned}$$

or eliminating y by the equation of the surface, (9)

$$(14) \quad z = \frac{14}{23} \frac{1}{x^3} \left(\frac{3x - 1}{2} \right)^2 + \frac{9}{46} \frac{3x - 1}{4},$$

whose projections are given by the broken lines in Figs. 2 and 3, respectively.

REGION OF TWO PHASES.

It is a familiar fact that while van der Waals' Equation, apparently applying to both the liquid and vapor phases, suggests only such transformations from one phase to the other as shall keep

the substance considered in one homogeneous phase, the actual transformations are usually effected by the discontinuous process of vaporization, during which the substance is non-homogeneous, being present in both the liquid and vapor phases at the same time. The actual isothermal of this process is represented in figure 1 for the temperature $\vartheta = \frac{3}{4}$ by a horizontal straight line, intersecting the ideal isothermal in three points. In Gibbs' Model, as Maxwell has shown,¹ such an isothermal is given by a line connecting the two points of tangency of a plane resting upon the model. We may then attempt to locate the boundary line separating the regions representing a single phase from those referring to the co-existence of two phases by either of two methods.

If the area under the actual and under the ideal isothermals is to be the same, if we call the volume of the liquid just ready to vaporize φ_1 , and that of the saturated vapor φ_2 , both at the temperature ϑ and the pressure Π , then

$$\int_{\varphi_1}^{\varphi_2} \Pi d\varphi = \int_{\varphi_1}^{\varphi_2} \pi d\varphi = \int_{\varphi_1}^{\varphi_2} \left(\frac{8\vartheta}{3\varphi - 1} - \frac{3}{\varphi^2} \right) d\varphi$$

or integrating,

$$\Pi(\varphi_2 - \varphi_1) = \frac{8}{3} \vartheta \log \frac{3\varphi_2 - 1}{3\varphi_1 - 1} + 3 \left(\frac{1}{\varphi_2} - \frac{1}{\varphi_1} \right)$$

and since van der Waals' equation itself still applies to the saturated vapor and liquid

$$\begin{aligned} \Pi &= \frac{8\vartheta}{3\varphi_2 - 1} - \frac{3}{\varphi_2^2} \\ \Pi &= \frac{8\vartheta}{3\varphi_1 - 1} - \frac{3}{\varphi_1^2} \end{aligned}$$

Three equations which are sufficient to give the relations between Π , φ_1 , φ_2 and ϑ if we can solve them. If we do obtain the solution, we can plot the locus of φ_1 and φ_2 in Fig. 1, and by algebraic transformations find the corresponding locus in Fig. 2, and Fig. 3.

Or, we may attempt the direct solution. The equation of the surface of our model (9), is of the form

¹ Theory of Heat, pp. 195-205.

$$z = me^y \left(\frac{3x-1}{2} \right)^{-r} + n \frac{3x-1}{x}$$

The equation of a plane is

$$z = ax + by + c.$$

If now the plane touch the surface at two points $x', y', z', x'', y'', z''$, the coördinates of these points must satisfy both equations, giving us

$$\begin{aligned} z' &= me^{y'} \left(\frac{3x'-1}{2} \right)^{-r} + n \frac{3x'-1}{x'}, \\ z'' &= me^{y''} \left(\frac{3x''-1}{2} \right)^{-r} + n \frac{3x''-1}{x''}, \\ z' &= ax' + by' + c, \\ z'' &= ax'' + by'' + c. \end{aligned}$$

The fact that the plane and surface are mutually tangent makes the slopes in the principal directions the same, or

$$\begin{aligned} \frac{\partial z'}{\partial x'} &= a = -\frac{3}{2} mre^{y'} \left(\frac{3x'-1}{2} \right)^{-1-r} + n \frac{3x'-1}{x'}, \\ \frac{\partial z''}{\partial x''} &= a = -\frac{3}{2} mre^{y''} \left(\frac{3x''-1}{2} \right)^{-1-r} + n \frac{3x''-1}{x''}, \\ \frac{\partial z'}{\partial y'} &= b = me^{y'} \left(\frac{3x'-1}{2} \right)^{-r}, \\ \frac{\partial z''}{\partial y''} &= b = me^{y''} \left(\frac{3x''-1}{2} \right)^{-r}. \end{aligned}$$

A point xyz which lies on the line connecting the two points of tangency will satisfy the two equations

$$\begin{aligned} \frac{y-y'}{x-x'} &= \frac{y'-y''}{x'-x''}, \\ \frac{z-z'}{x-x'} &= \frac{z'-z''}{x'-x''}, \end{aligned}$$

which gives us ten equations between which we may eliminate the six coördinates, $x', y', z', x'', y'', z''$ and the three constants a, b, c , still leaving an equation involving x, y, z , which is the equation of

the developable surface generated by a plane rolling on the model. The intersection of this surface with our model will be the line desired, separating the regions relating to one phase from that relating to two phases.

These two analytical methods of solution are here given for the sake of completeness. A direct and complete solution by algebraic methods does not seem possible, and lack of time has prevented my attempting approximate or graphical methods of solution. The horizontal portion of the isothermal $\vartheta = \frac{3}{4}$, in Fig. 1, was actually drawn by the method of trial, so as to make the areas included between it and the two segments of the ideal isothermal equal. This

Fig. 4.

enabled the line of separation to be drawn of approximately the right position and form.

DISCUSSION.

The lines of the various figures form a network which is to be considered as spread out over the surface of either model. These lines are lines of constant volume, constant pressure, constant temperature, and constant entropy. Fig. 1 is slightly less complex than Fig. 3, lacking the system of isentropics. Except for this there must be a one to one correspondence between the two networks, since they represent identically the same properties, thus the same lines pass through the critical point in each, and in each the same lines have points of tangency or intersection for the same values of x .

In the more specific discussion of the lines of Fig. 3, it is well to compare it with Fig. 4, which is taken from Maxwell.¹ An important difference which must be taken into account is that Fig. 3, refers only to the liquid and gaseous states, while Fig. 4 has also a region referring to the solid state.

The *isothermals* are indicated in Fig. 3 by the letter ϑ , in Fig. 4 by the letter T . An adiabatic or isentropic increase of volume is, so far as I know, under all circumstances accompanied by a fall of temperature. This property appears in Fig. 3 in which the isothermals slope downward to the right, but not in Fig. 4, in which they slope in general upward to the right, but occasionally have singular forms.

The *isopiestic*s are indicated in Fig. 3 by the letter π , in Fig. 4 by the letter P . The general form of a line of constant negative pressure is given by the curve $\pi = -1$. It has either two or no intersections with an isothermal, being tangent in one special case for each isopiestic. This property appears from Fig. 1. Each negative isopiestic passes off to infinity becoming asymptotic to a vertical line. The one shown has for its asymptote the line $x = \sqrt{3}$. The limiting case is the line $\pi = 0$. Like all the other isopiestics it is asymptotic to the line $x = 1/3$. It cuts all the isothermals twice or not at all, being tangent to one particular isothermal, and approaches parallelism to the isothermals, after cutting above them all, for $x = \infty$. This corresponds to the fact that in Fig. 1 the axis $\pi = 0$ is an asymptote to all the isothermals. Another limit-

¹ Theory of Heat, p. 207.

ing case is the line $\pi = 1$, which is tangent to the isothermal $\vartheta = 1$ at the critical point, and cuts every other isothermal once only. An example of an intermediate case is the isopiestic $\pi = \frac{1}{2}$, which cuts every isothermal either once or three times. The other case is illustrated by the lines $\pi = 2$ and $\pi = 3$ which cut every isothermal once only. All these properties appear from figure 1, and the fact that they also appear in Fig. 3, may be taken as a check upon the accuracy of the drawing. In general, the isopiestic for positive pressures slope downward to the right, although for very small pressures less than $\pi = \frac{1}{2}$ they may in the middle of the field slope up to the right. This does not appear in Fig. 4, which also does not exhibit the bunching of lines asymptotic to $x = \frac{1}{3}$. The line P_1 , which represents a negative pressure, is not entirely unlike the line $\pi = -1$.

The *Line of Instability*, represented by the broken line in Fig. 3, and by the dotted line in Fig. 4, has in the two cases not dissimilar properties, but in the former it dips below the level of the critical point, and passes off to infinity *horizontal*.

The line dividing the regions corresponding to a single phase from that corresponding to two co-existent phases is represented in both figures by a heavy line, which passes through the critical point and is there tangent to the critical isothermal, critical isopiestic, and the line of instability. It cuts all the isothermals below the critical twice, and all the positive isopiestic below the critical twice. In figure 3 it lies entirely between the isopiestic $\pi = 0$ and $\pi = 1$. At the critical point it passes below the level of the critical point, and passes off to infinity horizontal, as do the isothermals. It appears immediately from this diagram that the adiabatic expansion of a saturated vapor would result in partial condensation. Whether this line would in other regions at lower temperatures have such a form that adiabatic expansion would superheat a saturated vapor could only be told if we were able to obtain an analytic solution for the line, or plot it point by point. The matter is not of great importance, as we are dealing only with an equation, and not an actual substance.

The lines of Fig. 3 have all been plotted from their equations, with the exception of the one last discussed, which, however, we

have been able to draw with fair accuracy from our knowledge of its relations to the other lines of the figure. If the axes of coordinates of Fig. 4 are to be considered as similarly situated, the discrepancy between the two is very considerable, and very troublesome. If, however, the axes are to be taken as obliquely as they are drawn, v corresponding to x and φ to y , or if we regard Fig. 4 as a perspective drawing rather than a projection on one of the principal planes, the discrepancies, while by no means disappearing, become much less.

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