2-3 *P-v-T* SURFACE FOR AN IDEAL GAS

The equation of state of a *PvT* system defines a *surface* in a rectangular co-ordinate system in which P, v, and T are plotted along the three axes. A portion of this surface for an ideal gas is shown in Fig. 2–2. Every possible equilibrium state of an ideal gas is represented by a point on its *P-v-T* surface, and every point on the surface represents a possible equilibrium state. A quasistatic process, i.e., a succession of equilibrium states, is represented by a line on the surface. The full lines in Fig. 2–2 represent processes at constant temperature, or *isothermal* processes. The dotted lines represent *isochoric* processes, and the dashed lines, *isobaric* processes.

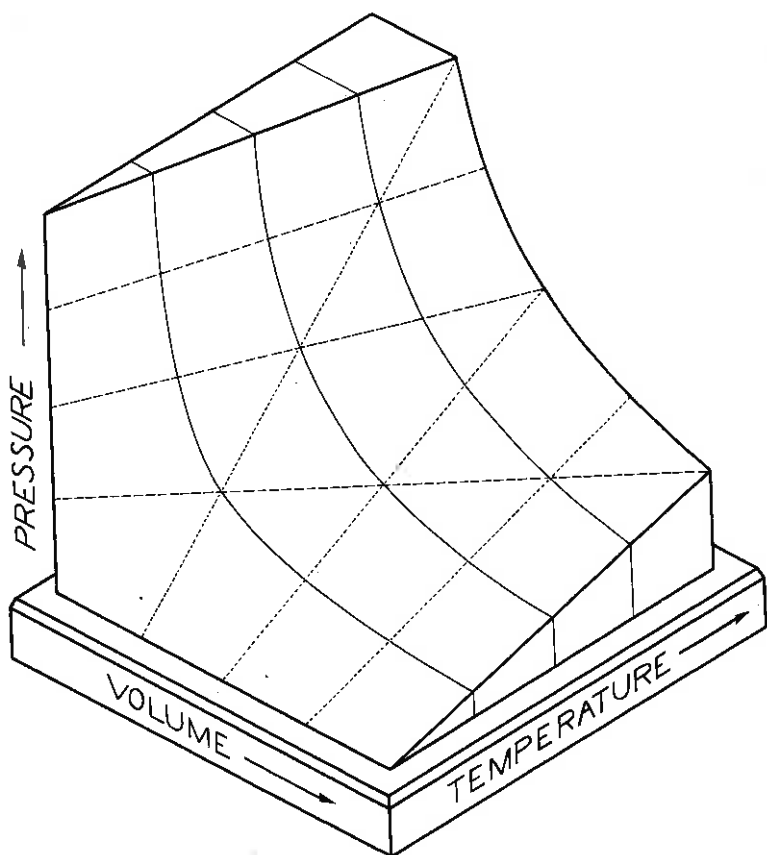Figures 2–3(a) and 2–3(b) are projections of the lines in Fig. 2–2 onto the *P-v* and *P-T* planes.

Fig. 2–2 *P-v-T* surface for an ideal gas.

2–4 EQUATIONS OF STATE OF REAL GASES

Many equations have been proposed which describe the P-v-T relations of real gases more accurately than does the equation of state of an ideal gas. Some of these are purely empirical, while others are derived from assumptions regarding molecular properties. Van der Waals*, in 1873, derived the following equation:

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT. \tag{2-8}$$

The quantities a and b are constants for any one gas but differ for different gases. Some values are listed in Table 2–1. We shall show in Chapter 10 that the term a/v^2 arises from the existence of intermolecular forces and that the term b is proportional to the volume occupied by the molecules themselves, but for the present we shall consider the equation as an empirical one.

Table 2–1 Constants a and b in van der Waals equation. P in N m^{-2}, v in m^3 kilomole^{-1}, T in kelvins, $R = 8.31 \times 10^3$ J kilomole^{-1} K^{-1}.

Substance	a (J m^3 kilomole^{-2})	b (m^3 kilomole^{-1})
He	3.44×10^3	0.0234
H$_2$	24.8	.0266
O$_2$	138	.0318
CO$_2$	366	.0429
H$_2$O	580	.0319
Hg	292	.0055

At sufficiently large specific volumes, the term a/v^2 becomes negligible in comparison with P, and b becomes negligible in comparison with v. The van der Waals equation then reduces to the equation of state of an ideal gas, which any equation of state must do at large specific volumes.

Figure 2–4 is a diagram of a portion of the P-v-T surface of a van der Waals gas, and Fig. 2–5 is a projection of a number of isotherms onto the P-v plane.
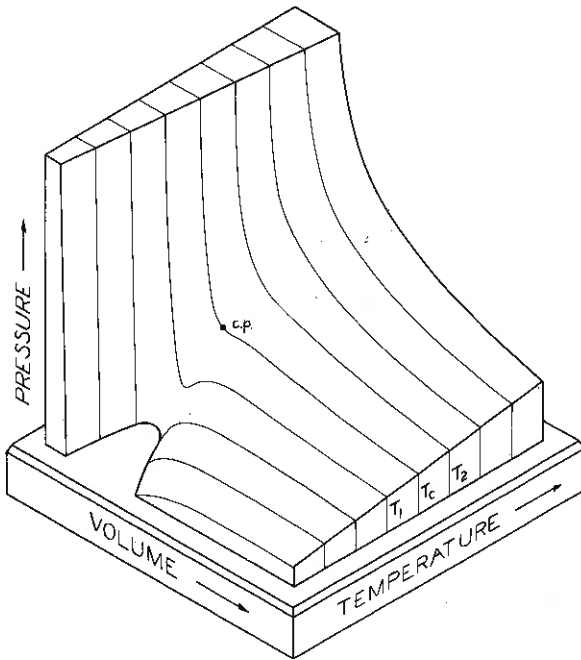
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* Johannes D. van der Waals, Dutch physicist (1837–1923).

Fig. 2–4 *P-v-T* surface for a van der Waals gas.
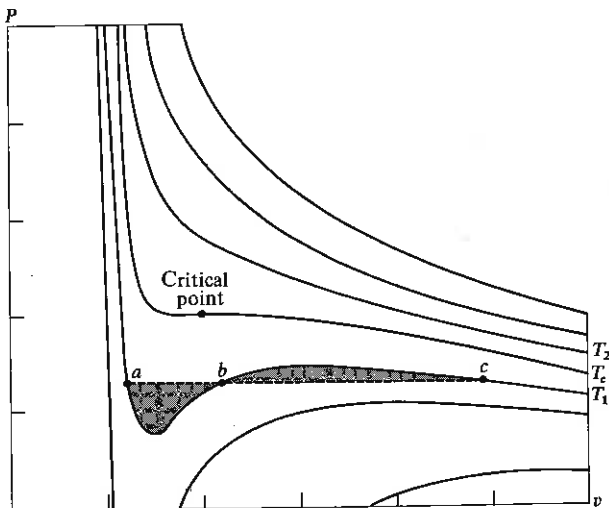

Fig. 2–5 Isotherms of a van der Waals gas.

regions lettered solid, liquid, and gas or vapor. (The distinction between a gas and a vapor will be discussed shortly.) In other regions, labeled solid-liquid, solid-vapor, and liquid-vapor, two phases can exist simultaneously in equilibrium, and along a line called the *triple line*, all three phases can coexist. As with the *P-v-T* surface for an ideal gas, any line on the surface represents a possible quasistatic process, or a succession of equilibrium states. The lines in Figs. 2–6 and 2–7 represent isothermal processes.
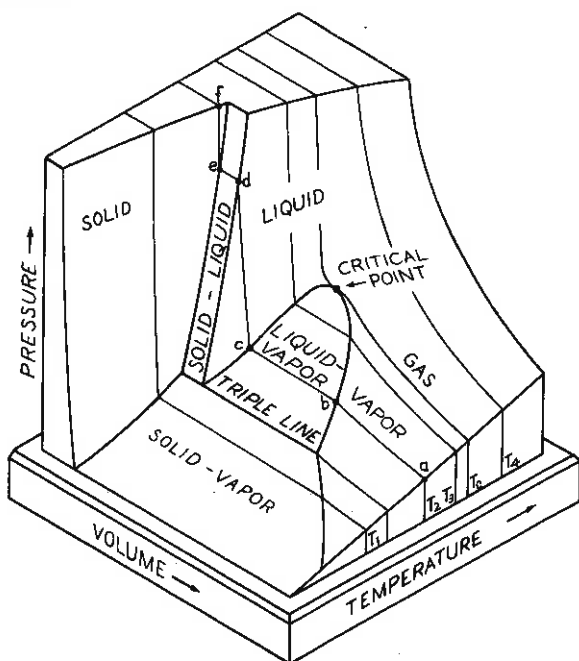

Fig. 2–6 *P-v-T* surface for a substance that contracts on freezing.

Those portions of a surface at which two phases can coexist are *ruled surfaces*. That is, a straight edge parallel to the *v*-axis makes contact with the surface at all points. Hence when the surfaces in Figs. 2–6 and 2–7 are projected onto the *P-T* plane, these surfaces project as lines. The projection of the surface in Fig. 2–6 onto the *P-T* plane is shown in Fig. 2–8(a), and that of the surface in Fig. 2–7 is shown in Fig. 2–9(a). The lines corresponding to values of pressure and temperature at which the solid and vapor phases, and the liquid and vapor phases, can coexist, always slope upward to the right. The line representing the equilibrium between solid and liquid slopes upward to the right in Fig. 2–8, but upward to the left in Fig. 2–9. We shall show in Section 7–6 that the former is characteristic of all substances that contract on freezing, the latter of substances (like water) that expand on freezing.
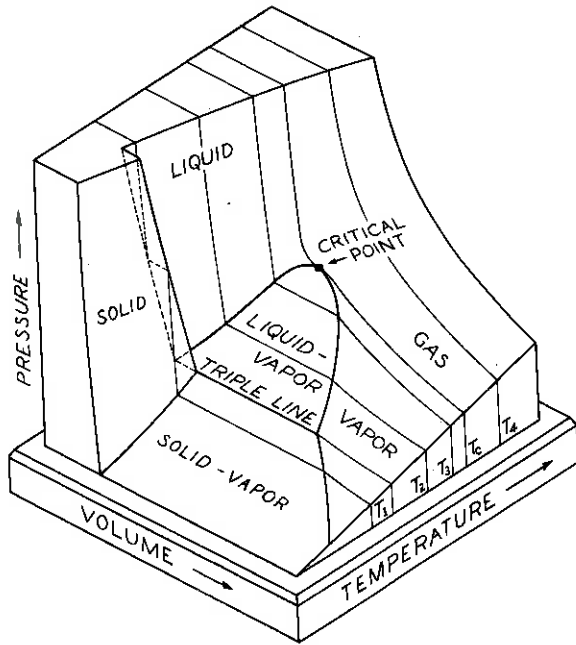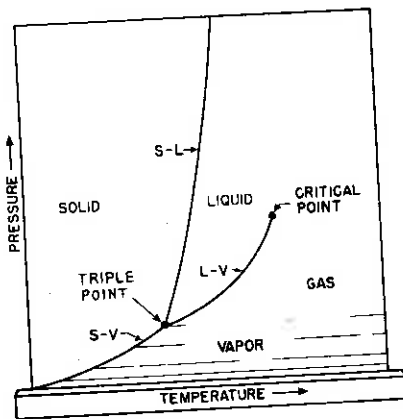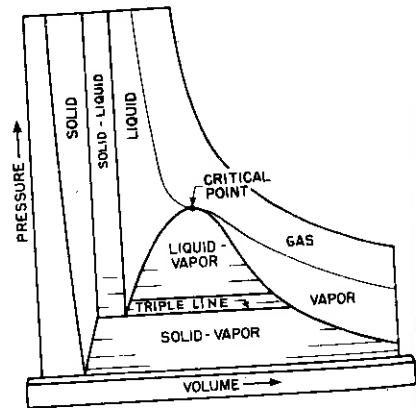
Fig. 2-7 *P-v-T* surface for a substance that expands on freezing.

Fig. 2-8 Projections of the surface in Fig. 2-6 onto (a) the *P-T* plane and (b) the *P-v* plane.
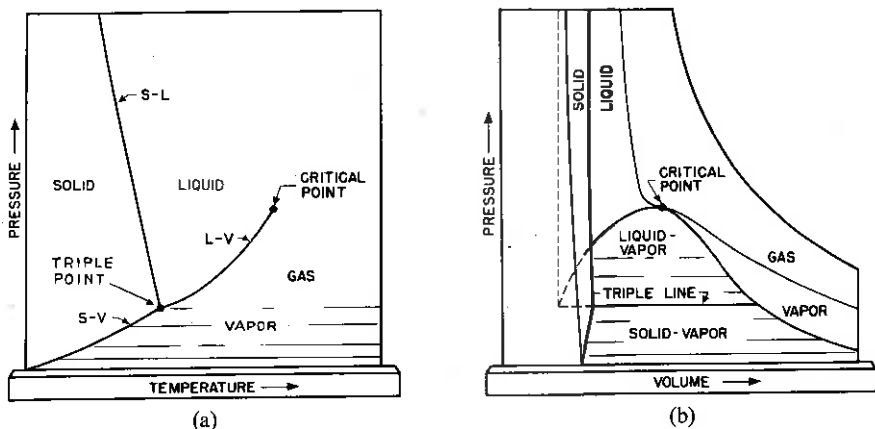
Fig. 2–9 Projections of the surface in Fig. 2–7 onto (a) the *P-T* plane and (b) the *P-v* plane.

The triple lines in Figs. 2–6 and 2–7 project as a point, called the *triple point*, in the *P-T* diagram. Triple-point data for a few common substances are given in Table 2–2. The triple-point temperature of water is the standard fixed point to which is assigned the arbitrary temperature of 273.16 K.

The projections of the surfaces in Figs. 2–6 and 2–7 onto the *P-v* plane are shown in Figs. 2–8(b) and 2–9(b). The surfaces can also be projected onto the *v-T* plane, but this projection is rarely used since all essential features of the surface can be shown in the first two projections.

Table 2–2 Triple-point data

Substance	Temperature, (K)	Pressure, (Torr)
Helium (4) (λ point)	2.186	38.3
Hydrogen (normal)	13.84	52.8
Deuterium (normal)	18.63	128
Neon	24.57	324
Nitrogen	63.18	94
Oxygen	54.36	1.14
Ammonia	195.40	45.57
Carbon dioxide	216.55	3880
Sulfur dioxide	197.68	1.256
Water	**273.16**	4.58