Chapter 2

Equations of State

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2.2 Equation of State of an Ideal Gas

$$PV = \frac{m}{M} RT \qquad (2.1)$$

m: mass of gas
M: molecular weight
R: universal constant
$(8.314 \times 10^3 \, \frac{\mathrm{J}}{\mathrm{kilomole \cdot K}})$

- Since $n \equiv \frac{m}{M}$ is the number of kilomoles of the gas, the equation of state of an ideal gas is

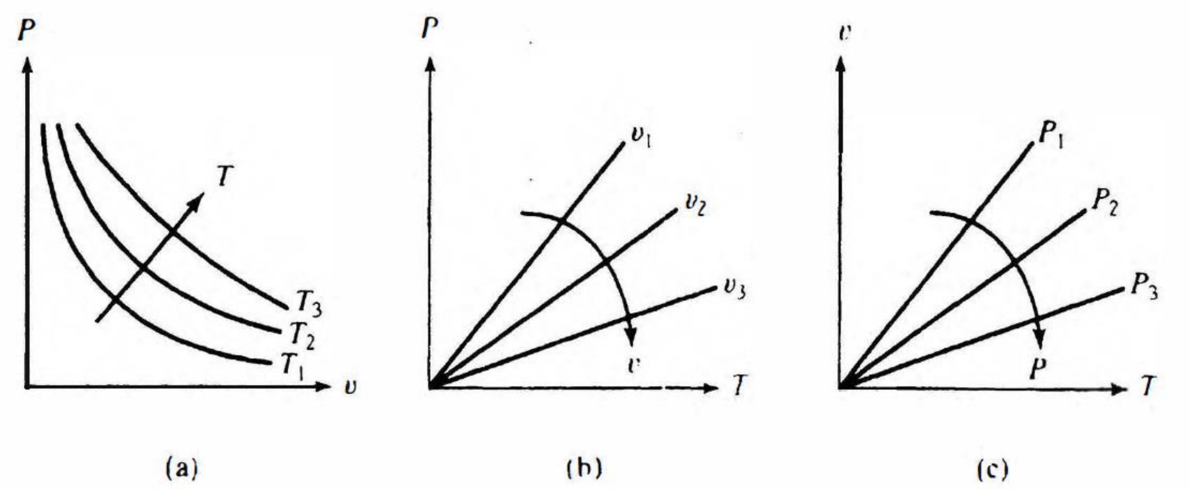
$$PV = nRT \qquad (2.2)$$

2.2 Equation of State of an Ideal Gas

- In Equation (2.2) we note that the extensive variable V divided by n, the number of kilomoles of the gas, is the specific volume v.

- Thus the equation of state can be written $Pv = RT$.

- The projections of the surface $f(P, v, T) = 0$ on the $P - v$ plane, $P - T$ plane, and the $v - T$ plane are shown in Figure 2.1



(a) (b) (c)

Figure 2.1 Diagrams for an ideal gas. (a) the isotherms are equilateral hyperbolae; (b) the isochores are straight lines; (c) the isobars are also straight lines.

2.3 Van Der Waals' Equation for a Real Gas

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT \qquad (2.3)$$

a and b: characteristic constants

- The term $\frac{a}{v^2}$ arises from the intermolecular forces due to the overlap of electron clouds.
- The constant b takes into account the finite volume occupied by the molecules.
- Multiplication of Equation (2.3) by v^2 yields the equation

$$Pv^3 - (Pb + RT)v^2 + av - ab = 0 \qquad (2.4)$$

2.3 Van Der Waals' Equation for a Real Gas

- Equation (2.4) is a cubic equation in v with three roots, only one of which needs to be real.

- In Figure 2.2 some isotherms calculated from the van der Waals equation have been drawn.

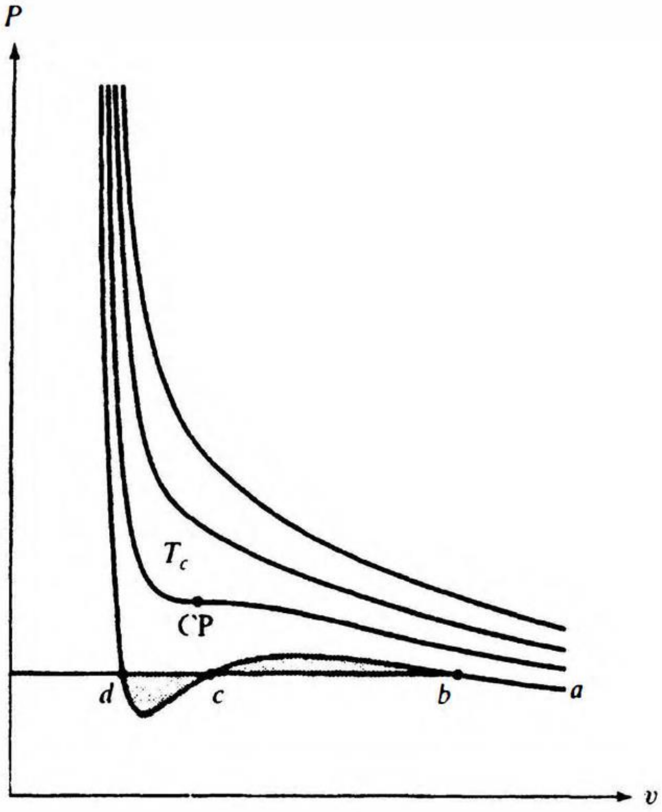


Figure 2.2 Isotherms for a Van Der Waals' gas.

2.4 $P - v - T$ Surfaces for Real Substances

- Figure 2.3 is a schematic diagram of the $P - v - T$ surface for a substance that contracts on freezing

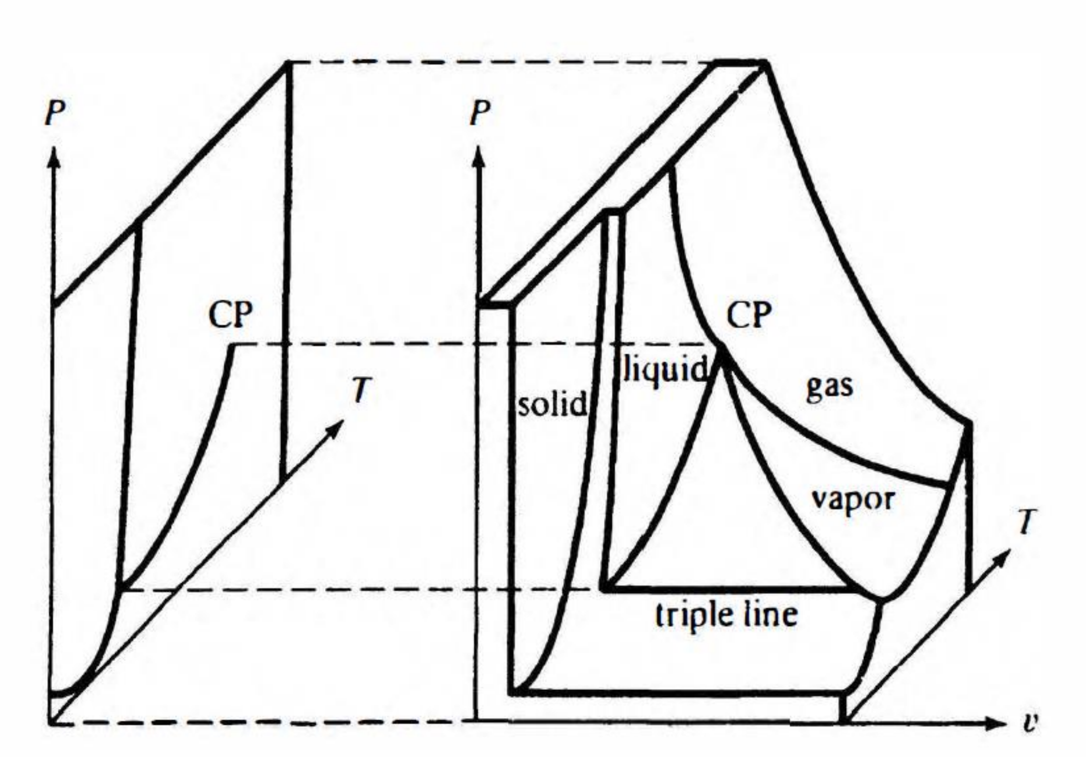
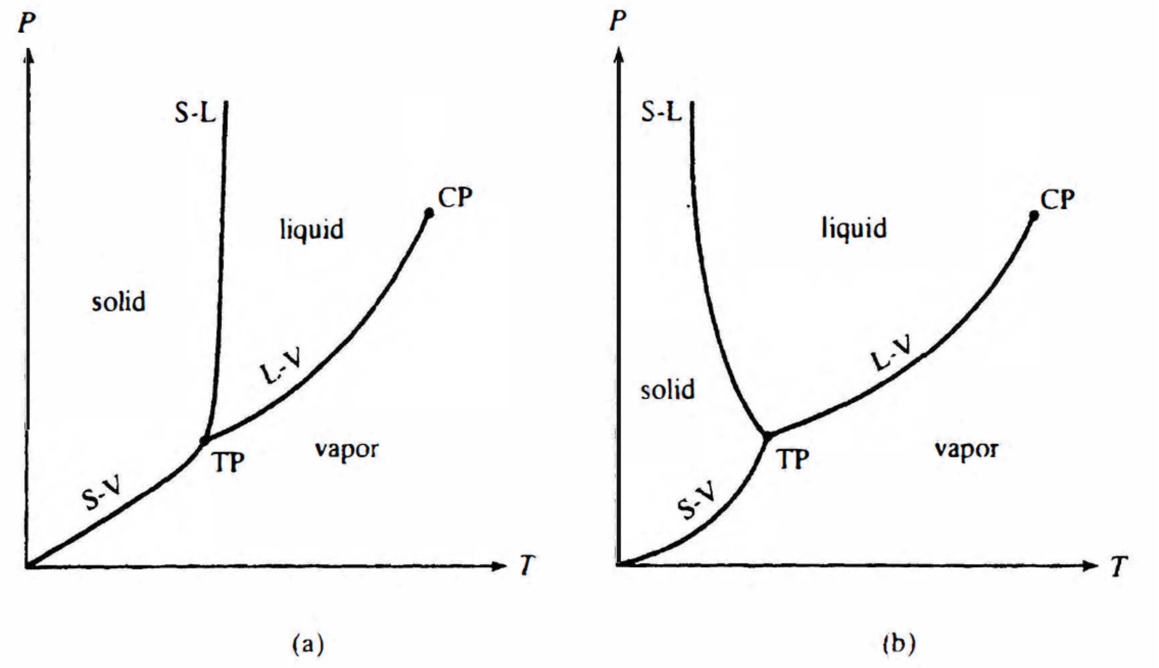


Figure 2.3 $P - v - T$ surface for a substance that contracts on freezing

2.4 $P - v - T$ Surfaces for Real Substances

- Notice the regions(solid, liquid, gas or vapor) in which the substance can exist in a single phase only.

- Elsewhere two phases can exist simultaneously in equilibrium, and along the so-called triple line, all three phases can coexist.



(a)

(b)

Figure 2.4 $P - T$ diagrams for (a) a substance that contracts on freezing; and (b) a substances that expands on freezing

2.5 Expansivity and Compressibility

- Suppose that the equation of state of a given substance is written in the form

$$v = v(T, P) \qquad (2.5)$$

- Taking the differential, we obtain

$$dv = (\frac{\partial v}{\partial T})_p dT + (\frac{\partial v}{\partial P})_T dP \qquad (2.6)$$

- The expansivity, or coefficient of volume expansion, is given by

$$\beta \equiv \frac{1}{v}(\frac{\partial v}{\partial T})_P \qquad (2.7)$$

- This is the fractional change of volume resulting from a change in temperature, at constant pressure.

2.5 Expansivity and Compressibility

- Similarly, the isothermal compressibility is defined as

$$k \equiv -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \qquad (2.8)$$

- This is the fractional change in volume as the pressure changes, with the temperature held constant.
- The negative sign is used since the volume always decreases with increasing pressure (at constant temperature)
- For an ideal gas, $v = RT/P$

$$\beta = \frac{1}{v}\left(\frac{R}{P}\right) = \frac{1}{T} \qquad (2.9)$$

$$k = -\frac{1}{v}\left(-\frac{RT}{P^2}\right) = \frac{1}{P} \qquad (2.10)$$

2.7 Specific heat

- **Specific heat:** the amount of heat required to change a unit mass of a substance by one degree in temperature

C_P, C_V → The properties we can measure

$$u = u(T, v) \qquad (2.11)$$

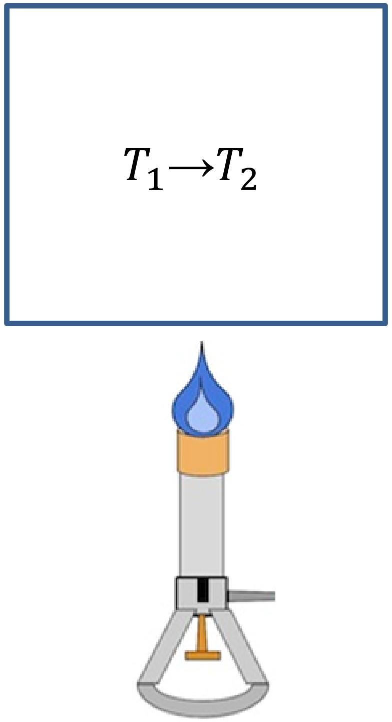
$$du = \underbrace{\frac{\partial u}{\partial T})_v}_{C_v} dT + \frac{\partial u}{\partial v})_T dv \qquad (2.12)$$

$$\begin{aligned} \delta Q &= \Delta U + \delta W \\ &= \Delta U + \cancel{Pdv} \\ &= \Delta U \qquad (2.13) \end{aligned}$$

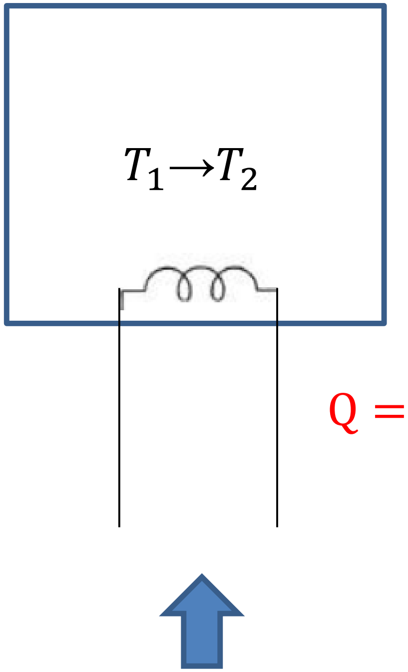
If there is no volume change (constant v)

2.7 Specific heat

V constant



V constant



$Q = i^2 R$

More easy to measure heat and internal energy in difference

$$C_v = \frac{\partial u}{\partial T})_v = \frac{\partial Q}{\partial T})_v \longrightarrow$$

C_v can be measured

2.7 Specific heat

$$h \equiv u + pv$$

$$= h(T, P) \qquad (2.14)$$

$$dh = \underbrace{\frac{\partial h}{\partial T})_P}_{C_P} dT + \frac{dh}{dp})_T dP \qquad (2.15)$$

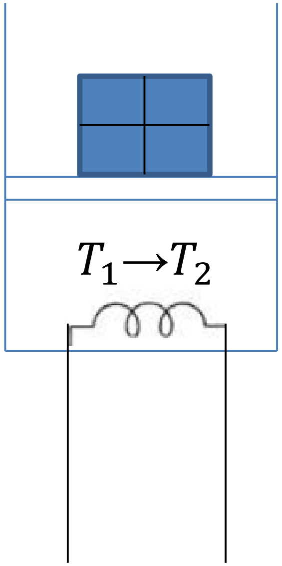
$$\delta Q)_{Idea} = Tds = du + Pdv$$

$$= dh - \cancel{vdP} \qquad (2.16)$$

If there is no pressure change
(constant P)

2.7 Specific heat

Constant pressure



Amount of heat added = Δh

$$C_P \equiv \frac{\partial h}{\partial T})_P = \frac{\partial Q}{\partial T})_P \longrightarrow$$

C_P can be measured

2.8 Maxwell equation

$$du = Tds - Pdv \qquad (2.17)$$

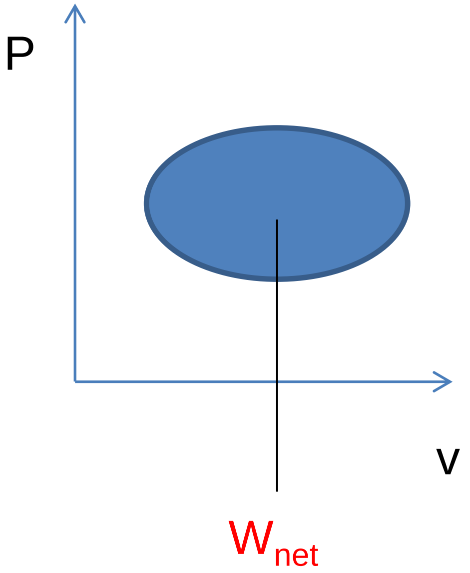
$$u = u(s, v) \qquad (2.18)$$

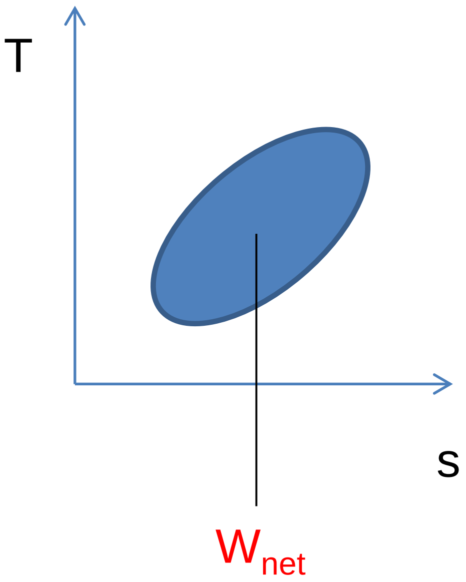
$$du = \underset{T}{\boxed{\frac{\partial u}{\partial s}}})_v ds + \underset{P}{\boxed{\frac{\partial u}{\partial v}}})_s dv \qquad (2.19)$$

$$\frac{\partial}{\partial v}(\frac{\partial u}{\partial s})_h = \frac{\partial}{\partial s}(\frac{\partial u}{\partial h})_s \longrightarrow \frac{\partial T}{\partial v})_s = -\frac{\partial p}{\partial s})_v \qquad (2.20)$$

2.8 Maxwell equation

$$J = \frac{\partial(P,v)}{\partial(T,s)} = 1$$





Jacobian

$$dxdy = rdrd\theta$$

$$x = rcos\theta$$

$$y = rsin\theta$$

$$\frac{\partial(T,s)}{\partial(v,s)} = \frac{\partial(P,v)}{\partial(v,s)} = -\frac{\partial(P,v)}{\partial(s,v)} = -\frac{\partial P}{\partial s}\Big)_v$$