Advanced Thermodynamics (M2794.007900)

Chapter 2

Equations of State

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2.2 Equation of State of an Ideal Gas

$$PV = \frac{m}{M}RT \tag{2.1}$$

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

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

$$PV = nRT \tag{2.2}$$



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



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

$$\left(\boldsymbol{P} + \frac{a}{\nu^2}\right)(\boldsymbol{\nu} - \boldsymbol{b}) = \boldsymbol{R}\boldsymbol{T}$$
(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

$$Pv^{3} - (Pb + RT)v^{2} + av - ab = 0$$
 (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.



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

$$v = v(T, P) \tag{2.5}$$

• Taking the differential, we obtain

$$d\nu = \left(\frac{\partial \nu}{\partial T}\right)_p dT + \left(\frac{\partial \nu}{\partial P}\right)_T dP \tag{2.6}$$

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

$$\beta \equiv \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P \tag{2.7}$$

• 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

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

- 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

$$\beta = \frac{1}{\nu} \left(\frac{R}{P}\right) = \frac{1}{T}$$

$$k = -\frac{1}{\nu} \left(-\frac{RT}{P^2}\right) = \frac{1}{P}$$
(2.9)
(2.10)



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

 C_P , $C_V \rightarrow$ The properties we can measure

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

$$du = \left(\frac{\partial u}{\partial T}\right)_{v} dT + \frac{\partial u}{\partial v}\right)_{T} dv$$
(2.12)

$$\delta Q = \Delta U + \delta W$$
(2.12)

$$\delta Q = \Delta U + \delta W$$
If there is no volume change (constant v)

$$= \Delta U$$
(2.13)







$$h \equiv u + pv$$

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

$$dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \frac{dh}{dp}\right)_T dP$$
(2.15)

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

= $dh - vdP$ (2.16)

If there is no pressure change (constant P)



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

$$du = Tds - Pdv \tag{2.17}$$

$$u = u(s, v)$$
(2.18)
$$du = \left(\frac{\partial u}{\partial s}\right)_{v} ds + \left(\frac{\partial u}{\partial v}\right)_{s} dv$$
(2.19)
$$T - P$$

$$\frac{\partial^2 U}{\partial v \partial s} = \left(\frac{\partial T}{\partial v}\right)_s = \frac{\partial^2 U}{\partial s \partial v} = -\left(\frac{\partial P}{\partial s}\right)_v \longrightarrow \frac{\partial T}{\partial v}_s = -\frac{\partial P}{\partial s}_v$$
(2.20)



2.8 Maxwell equation



