Thermodynamic Potentials (Chapter 17)

- Consider the four thermodynamic potentials:
  - Internal energy U
  - Enthalpy H
  - Helmholtz Free Energy A
  - Gibbs Free Energy G
- Each of these may be shown to be a Legendre Transform of the other:

$$H = U + pV$$

$$A = U - TS$$

$$G = H - TS = U + pV - TS$$

- The differentials of each of these may be written:

$$dU = TdS - pdV \text{ (The Master Equation of Thermodynamics)}$$

- (Continued)

$$dH = TdS + Vdp$$

$$dA = -SdT - pdV$$

$$dG = -SdT + Vdp$$

- Thus each of the thermodynamic potentials may be considered in terms of their natural variables:

$$U(S, V)$$

$$H(S, p)$$

$$A(T, V)$$

$$G(T, p)$$

- From the total differentials of each of these and utilizing the fact that thermodynamic potentials are state functions and have exact differentials, the Maxwell relations may be derived:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p$$

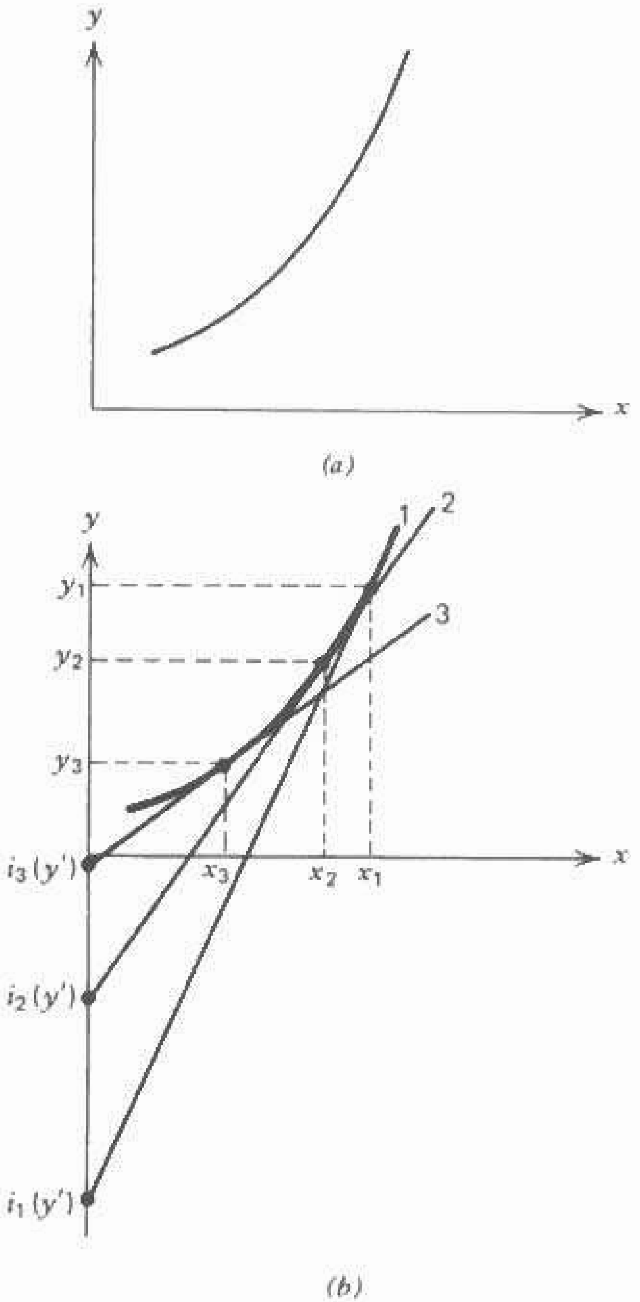

Figure 17.1 Diagram illustrating a Legendre transformation (see text).

Conditions for Stable Equlibrium

- Systems not at equilibrium will move spontaneously toward equilibrium in accordance with the Second Law of Thermodynamics.
  - For an isolated system:

$$dS_{sys} > 0$$

  - If a system is not at equlibrium, then the surroundings must be considered.

$$dS_{tot} = dS_{sys} + dS_{surr} > 0$$

$$\text{or } dS_{sys} > -dS_{surr}$$

$$\text{or } dS_{sys} > \frac{dq_{rev}}{T_{surr}}$$

- If only pV work is involved and since $đq = dU - đw$,

$$dS_{sys} > \frac{dU_{sys}}{T_{surr}} + p_{ext}dV$$

- This may be rewritten as:

$$T_{surr}dS_{sys} > dU_{sys} + p_{ext}dV$$

  which gives an expression for a system moving spontaneously to a new equilibrium.

- If the system is at equilibrium, $T_{surr} = T$ and $p_{ext} = p$, then

$$TdS = dU + pdV$$

  which is the Master Equation.

- The conditions for equilibrium and spontaneous change may be considered in terms of the constraints.
  - Recall that constraints describe how a system is in contact with the surroundings.
- Consider the case of constant volume and constant entropy.

$$dV = 0; \; dS = 0$$

  - Then the condition for spontaneous change:

$$dS_{sys} > \frac{dU_{sys}}{T_{surr}} + p_{ext} dV$$

becomes:

$$0 > dU_{V,S} \text{ or } dU_{V,S} < 0$$

and internal energy is minimized.

- Consider the case of constant volume and constant internal energy:

  $$dV = 0; \; dU = 0$$

  then

  $$dS_{V,U} > 0$$

  .
- These constraints are consistent with:
  - A closed isolated system
  - A system undergoing an adiabatic reversible process at constant volume.
- Consideration of other constraints will need to be in terms of the appropriate thermodynamic potential.
- Enthalpy H will be used to consider constant S and p.

- Helmholtz free energy will be used to consider constant T and V.
- Gibbs free energy will be used to consider constant T and p.
- Consider enthalpy

  $$H = U + PV$$

  and its differential

  $$dH = dU + pdV + Vdp$$

- The condition for spontaneity:

  $$T_{surr}dS_{sys} > dU_{sys} + p_{ext}dV$$

  becomes $T_{surr}dS_{sys} > dH - pdV - Vdp + p_{ext}dV$

- If p and S are constant, then $dp = 0$, $dS = 0$, and $p = p_{ext}$.
- Thus $dH_{S,p} < 0$.
- Consider Helmholtz free energy.

  $$A = U - TS$$

  and its differential:

  $$dA = dU - TdS - SdT$$

  .
- The condition for spontaneity is:

  $$T_{surr} dS_{sys} > dU_{sys} + p_{ext} dV$$

- In terms of the Helmholtz free energy, this becomes:

$$T_{surr} dS_{sys} > dA + TdS + SdT - p_{ext} dV$$

- At constant T, $T_{surr} = T$ and $dT = 0$
- At constant V, $dV = 0$.
- Therefore:

$$0 > dA_{T,V}$$

- Consider Gibbs free energy:

$$G = U - TS + pV$$

and its differential:

$$dG = dU - TdS - SdT + pdV + Vdp$$

- The condition for spontaneity:

$$T_{surr} dS_{sys} > dU_{sys} + p_{ext} dV$$

becomes:

$$T_{surr} dS_{sys} > dG + TdS + SdT + pdV + Vdp - p_{ext} dV$$

- At constant T, $T_{surr} = T$ and $dT = 0$.
- At constant p, $p_{ext} = p$ and $dp = 0$.
- Therefore:

$$0 > dG_{T,p}$$

- Thus the condition for sponaneity, that S be maximized becomes that the thermodynamic potentials be minimized under the corresponding constraints.

- The conditions for spontaneity under different constraints are:

$$dS_{U,V} > 0$$

$$dU_{V,S} < 0$$

$$dH_{P,S} < 0$$

$$dA_{T,V} < 0$$

$$dG_{T,P} < 0$$

Spontaneity and Work (Chapter 19)

- Of particular interest are spontaneous process that lead to work being transferred to the surroundings.
  - What is the maximum amount of work that can be transferred to the surroundings under different constraints?

- Consider a closed system with two parts, I and II:
  - Part I contains n moles of a pure substance in volume V at temperature T and pressure p.
  - Part II contains dn moles of the same substance at T and p with a volume vdn where v is the molar volume.
  - The boundary between I and II is deformable.
    - This means that V can change and an infinitesimal change in V is accompanied by an infinitesimal change in p.
  - Part II is connected to a piston that allows work to be done on or by the dn moles of substance in Part II.
  - The nature of the boundary between Part I and Part II of the system may be such that it is permeable.

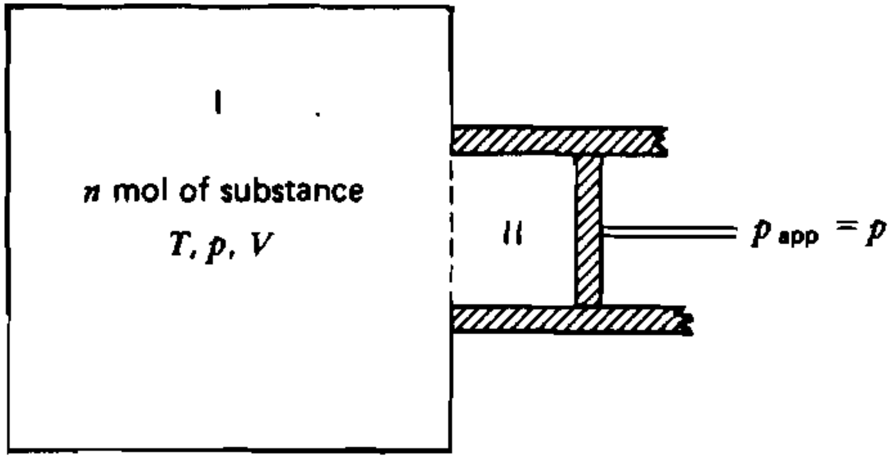

Figure 19.1 Schematic representation of a system with two parts. In part I, which has volume V, are n mol of substance at T and p. In part II are dn mol of the same substance, also at T and p. The piston shown permits the volume of part II to be decreased to zero. The dashed line indicates the boundary between parts I and II. Heat can be transferred to part I, but not to part II, and part I can do work on the surroundings.

- Consider two states of the system:
    - In the initial state of the system, the total internal energy is:
      $$nu + udn$$
      where u is the molar internal energy of the system.
    - In the final system, work has been done on Part II of the system to drive reversibly and isothermally at constant pressure dn moles into Part I of the system, changing the volume of Part I from V to $V + dV$.
    - The work that was done on Part II is $pvdn$.
    - Therefore the work done by Part I of the system is pdV on the surroundings.
    - This must be accompanied by at transfer of heat $đq$ from the surroundings to maintain the constant temperature.

- The internal energy of the final state for Part I is:

$$nu + dU$$

- The internal energy of the entire system is described as:

$$dU - u\ dn = đq - p\ dV + pv\ dn$$

- Molar enthalpy h is defined as $h = u + pv$
- Therefore

$$dU = đq + hdn - pdV$$

  - This a form of the first law when transfer of mass is allowed.
- Similarly, when mass transfer is allowed the second law becomes:

$$ns + sdn$$

- Entropy changes are associated with the transfer of mass, the work done, and the heat transferred.
- The dn moles of substance are transferred isothermally and reversibly, therefore:

$$dS - sdn = \frac{\text{đ}q}{T} = \frac{dU}{T} - \frac{h}{T}dn + \frac{p}{T}dV$$

- Molar Gibbs free energy is defined as:

$$g = h - Ts$$

- The master equation may be generalized to include mass transfer:

$$dU = TdS - pdV + gdn$$

  and the molar free energy of a substance g may be identified as the chemical potential of that substance.

- This may be applied to any one component system, including multiphase systems.
- An isolated system at equilibrium is one in which the entropy has been maximized.
  - Any perturbation of this system while maintaining the original constraints results in a decrease or no change in entropy.
- Gibbs' statements of the criteria for equilibrium are:
  “For the equilibrium of any isolated system it is necessary and sufficient that, in all possible variations of the state of the system that do not alter its energy, the variation of its entropy shall either vanish or be negative.”
  “For the equilibrium of any isolated system it is necessary and sufficient that, in all possible variations of the state of the system that do not alter its entropy, the variation of its energy shall either vanish or be positive.”

- Consider a one component, two phase isolated system.
- Therefore:
  - The internal energy is constant: $U^{(1)} + U^{(2)} = U$.
  - The total volume is constant: $V^{(1)} + V^{(2)} = V$.
  - The total mass of the one component in the system is constant: $n^{(1)} + n^{(2)} = n$.
- If any other constraint is altered, $(\delta S)_{U,V,n} \leq 0$ must be obeyed.
- The change in entropy may be considered for each phase:

$$T^{(1)} dS^{(1)} \leq dU^{(1)} + p^{(1)} dV^{(1)} - g^{(1)} dn^{(1)}$$

$$T^{(2)} dS^{(2)} \leq dU^{(2)} + p^{(2)} dV^{(2)} - g^{(2)} dn^{(2)}$$

- The total change in entropy is:

$$dS = dS^{(1)} + dS^{(2)}$$

- Therefore

$$dS \leq \frac{dU^{(1)}}{T^{(1)}} + \frac{dU^{(2)}}{T^{(2)}} + \frac{p^{(1)}}{T^{(1)}} dV^{(1)} + \frac{p^{(2)}}{T^{(2)}} dV^{(2)}$$

$$- \frac{g^{(1)}}{T^{(1)}} dn^{(1)} - \frac{g^{(2)}}{T^{(2)}} dn^{(2)}$$

- But by conservation of mass, volume, and mass:

$$dU^{(1)} = -dU^{(2)}$$

$$dV^{(1)} = -dV^{(2)}$$

$$dn^{(1)} = -dn^{(2)}$$

- Therefore:

$$dS \leq \left[\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}}\right] dU^{(1)} + \left[\frac{p^{(1)}}{T^{(1)}} - \frac{p^{(2)}}{T^{(2)}}\right] dV^{(1)}$$

$$- \left[\frac{g^{(1)}}{T^{(1)}} - \frac{g^{(2)}}{T^{(2)}}\right] dn^{(1)}$$

- In order for equilibrium to be attained, the coefficients of $dU^{(1)}$, $dV^{(1)}$, and $dn^{(1)}$ must vanish.
  - This can only happen if:

$$T^{(1)} = T^{(2)}$$

$$p^{(1)} = p^{(2)}$$

$$g^{(1)} = g^{(2)}$$

- Now consider varying the constraints (U, V, n).
  - If $dV^{(1)} > 0$, then in order for $dS < 0$,

$$\frac{p^{(1)}}{T^{(1)}} - \frac{p^{(2)}}{T^{(2)}} < 0$$

  .
  - If $T^{(1)} = T^{(2)}$, then $p^{(1)} < p^{(2)}$.
- If each of the constraints were varied one at a time, then:

$$T^{(1)} > T^{(2)} \text{ when } dU^{(1)} > 0$$

$$\frac{p^{(1)}}{T^{(1)}} < \frac{p^{(2)}}{T^{(2)}} \text{ when } dV^{(1)} > 0$$

$$\frac{g^{(1)}}{T^{(1)}} > \frac{g^{(2)}}{T^{(2)}} \text{ when } dn^{(1)} > 0$$

- Thus the conditions for spontaneity require that in approaching equilibrium:
  - Energy flows from higher to lower temperature.
  - Volume flows from higher to lower pressure.
  - Matter flows from higher to lower chemical potential (molar Gibbs energy).
- Displacement of a system from equilibrium requires that work be done on the system.
- The return to the original state means that work can be done on the surroundings.
  - What is the maximum amount of work that can be done on the surroundings under various constraints?
  - If the system is to do work on the surroundings, it is not isolated from the surroundings.

- A system may be constrained to have constant temperature by being in contact with a thermal reservoir.
- A system may be constrained to constant pressure by a piston in contact with the surroundings.
- As previously indicated, work must be done to displace an isolated system from equilibrium.

$$w_{inv} = -\int T dS$$

since in an isolated system, internal energy U does not change.

  - By the mean value theorem:

$$w_{inv} = -\overline{T} \int dS = -\overline{T} \Delta S_{inv}$$

- Since w_{inv} displaced the system from equilibrium, the entropy has decreased:

$$\Delta S_{inv} < 0 \text{ and } w_{inv} > 0$$

- Consider now an isolated system constrained to be at constant entropy.
  - A reversible adiabatic path will not change the entropy, but can change the internal energy.
  - The work required to displace the system from equilibrium is:

$$w_{inv}^{S} = \int dU$$

and the internal energy has increased, therefore:

$$w_{inv}^{S} > 0$$

- Consider an isolated system.
- Displacement from equilibrium would involve the imposition of a constraint and w_{inv}.
- If this constraint was removed, the isolated system would spontaneously return to equilibrium.
- If the system were coupled to the surroundings then up to $-w_{inv}$ would be available to do work on the surroundings.
- If this coupling maintains the constraints of the original isolated system and permitted the work to be done reversibly, then the maximum work ($-w_{inv}$) would be done.
- Consider a system that is not isolated.
    - The constraints determine by how it is connected to the surroundings.

- For an adiabatic process $w = \Delta U$.
- Consider a closed system in contact with a reservoir at temperature T_R.
    - This system undergoes a change from state 1 to state 2.
    - By the first law $w = \Delta U - q$ or $đw = dU - đq$.
    - Consider a reversible path, so that the infinitesimal heat transfer $đq$ is reversible.
    - This is accomplished by use of a reversible engine between the system and the heat reservoir.
    - This engine operates between T_R and T while $đq$ is transferred.
    - The work done by the reversible engine is:

$$đw_R = \left(\frac{T - T_R}{T}\right) đq$$

- Recall that $dS = đq_{rev}/T$.
- Generally:

$$dS \geq \frac{đq}{T}$$

- If a different engine is used for each infinitesimal segment of the path from 1 to 2, then:

$$\Delta S \geq \int_1^2 \frac{đq}{T}$$

  where T is the source temperature and differs from T_R, the constant temperature reservoir with which the system is in contact.
- Therefore:

$$T_R \Delta S - T_R \int_1^2 \frac{đq}{T} \geq 0$$

- This may be rearranged as:

$$0 \geq -T_R \Delta S + T_R \int_1^2 \frac{đq}{T}$$

- The first law may be rewritten as:

$$w = \Delta U - q = \Delta U - \int_1^2 \frac{T}{T} dq$$

- Combining this with the above gives:

$$w \geq \Delta U - T_R \Delta S - \int_1^2 \left(\frac{T - T_R}{T} \right) đq$$

- But:

$$w_R = \int_1^2 \left(\frac{T - T_R}{T} \right) đq$$

- Therefore
$$w + w_R \geq \Delta U - T_R \Delta S$$
- If all processes are reversible than the equal sign holds and the maximum work that can be done by the system is:
$$w_{max} = w + w_R$$
(Recall that work done by the system is negative).
- If the volume of the system is held constant, then the only work that can be done by the system is done through the reversible engines.
- Therefore $w_{x,max} = \Delta U - T_R \Delta S = \Delta A$ and the Helmholtz free energy is the maximum work done by the system when V is held constant.

- Consider the system at fixed pressure instead of fixed volume.
- This means that the system can do pressure volume work on the surroundings in the amount $-p\Delta V$.
- Therefore the maximum non-expansion work that can be done is:
$$\begin{aligned} w_{x,max} &= \Delta U - p\Delta V - T_R \Delta S \\ &= \Delta H - T_R \Delta S = \Delta G \end{aligned}$$
- The Gibbs free energy is the maximum non-pressure volume work done by the system when p is held constant.
- Note that the temperature of the initial and final state is T_R but may be alloved to vary along the path.
- If a process is not adiabatic, $T_R \Delta S$ is the difference between the energy change and the amount of energy available for work.

- The foregoing may now be considered in the context of a system displaced from equilibrium.
- This displacement in done bu doing work to impose a new constraint.
- If this new constraint is removed and the system coupled appropriately to the surroundings, then $-w_{inv}$ could be used to do work.
- For a system that is not isolated, the nature of the equilibrium is determined by the nature of the reservoirs with which the system is in contact.
- The criteria that describe the equilibrium state are related to the maximum work that can be done by the system $-w_{inv}^{C}$ where the superscript C describes the constraints.

- Systems of interest are closed and are in contact with reservoirs that fix intensive variables such as p and T.
- Consider a system of interest, system I.
    - This system is embedded in an infinitely large medium of temperature T_0 and pressure p_0.
        - Any change in the state of system I will not change T_0 and p_0.
    - This surrounding medium is bounded by a rigid adiabatic envelope.
    - Therefore the composite system, consisting of system I and the surrounding medium, may be regarded as isolated from the surroundings.
    - Consider the greatest amount of work that can be done on the embedding medium when system I changes state from 1 to 2.

- Since p and T are constant,

$$w'_{max} = \Delta U + p\Delta V - T\Delta S = \Delta G$$

- If the system is at equilibrium, the $\Delta G = w'_{max} = 0$.
- Since

$$dG = -SdT + Vdp$$

  any process at constant pressure and temperature does not change the Gibbs Free energy.
- Therefore w'_{max} is the greatest possible work that can be done if the system changes from 1 to 2 by removal of a constraint.
- Consider a reversible process that drives the system to a new state.
  - This will involve application of a new constraint.

- If that constraint is removed, this new state will be unstable and will return spontaneously to the original state,

$$w_{inv}^{C} = -w'_{max}$$

$$w'_{max} < 0$$

$$w_{inv}^{C} > 0$$

- Therefore

$$(\Delta U + p_0 \Delta V - T_0 \Delta S)_{inv} > 0$$

and the minimum value of G at equilibrium is defined by:

$$(\delta U + p_0 \delta V - T_0 \delta S)_{p_0, T_0} = 0$$

for states of the system that have the original constraints.

- But $p_0\delta V = -\delta w^C$, the pV work associated with the constraint of pressure.
- Generalizing to an arbitrary set of constraints:

$$(\Delta U - w^C - \int TdS)_{inv} > 0$$

$$\text{and } (\delta U - \delta w^C - T\delta S)_C = 0$$

  - The actual function that is maximized or minimized depends on the actual constraints.
  - For example, if mass, energy and volume are fixed:

$$-\int TdS > 0 \quad \text{or} \quad \Delta S < 0.$$

and a displacement from equilibrium would decrease the entropy.

- If entropy, volume, and mass are fixed:

  $$\Delta U > 0$$

  is required for a displacement from equilibrium.
- If S, p, and n are fixed:

  $$\Delta U - w^C > 0$$

  $$\text{or } \Delta H > 0$$

  is required for displacement from equilibrium.
- If T, V, and n are fixed:

  $$\Delta U - \int T dS > 0 \text{ or } \Delta A > 0$$

  is required for displacement from equilibrium.

- If T, p, and n are fixed:

$$\Delta U - w^C - \int T dS > 0$$

$$\text{or } \Delta G > 0$$

is required for displacement from equilibrium.

Stability of one-component systems

- The general condition:

$$(\delta U - \delta w^C - T\delta S)_C = 0$$

is a necessary but not sufficient condition for equilibrium.
  - This condition is met by a maximum, a plateau, or a local minimum (see figure 19.2).

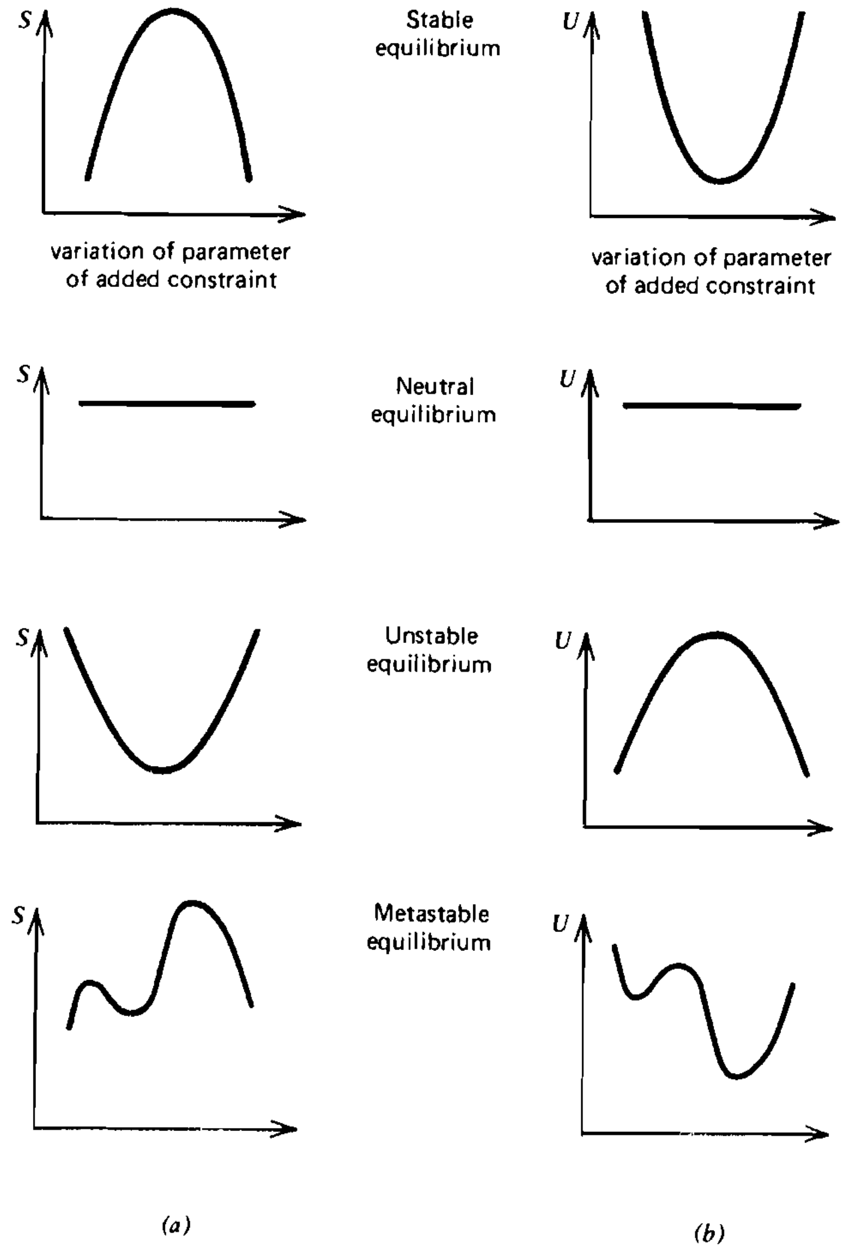

Figure 19.2 Schematic representations of the variations of S and U with change of added constraint for the four classes of equilibrium.

- A system is in stable equilibrium if displacement to a new state followed by release of a constraint always returns the system to its original state.
- A system is in neutral equilibrium if other states of the same energy, volume, and mass have the same entropy.
- A system is in unstable equilibrium if displacement to a new state followed by release of a constraint never returns the system to its original state.
- A system is in metastable equilibrium if displacement to a nearby state followed by release of a constraint returns the system to its original state but a larger displacement does not return the system to its original state.
- All of the forgoing discussion about available work was in the context of either stable or metastable equilibrium.

- The removal of a constraint that leads to a spontaneous reversible process is associated with a neutral equilibrium.
- For systems that have a stable equilibrium, the following is observed to be true:
  - An increase of external pressure at constant temperature and mass must lead to a decrease of volume.
  - The addition of heat at constant pressure and volume must lead to an increase of temperature.
- The implications of this definition for stable equilibrium will be considered in the context of the virtual variation of the system in Figure 19.3 which has two identical subvolumes.
  - The partition is moved from the point at which $\Delta V = 0$ and $\Delta S = 0$ to the position of interest.

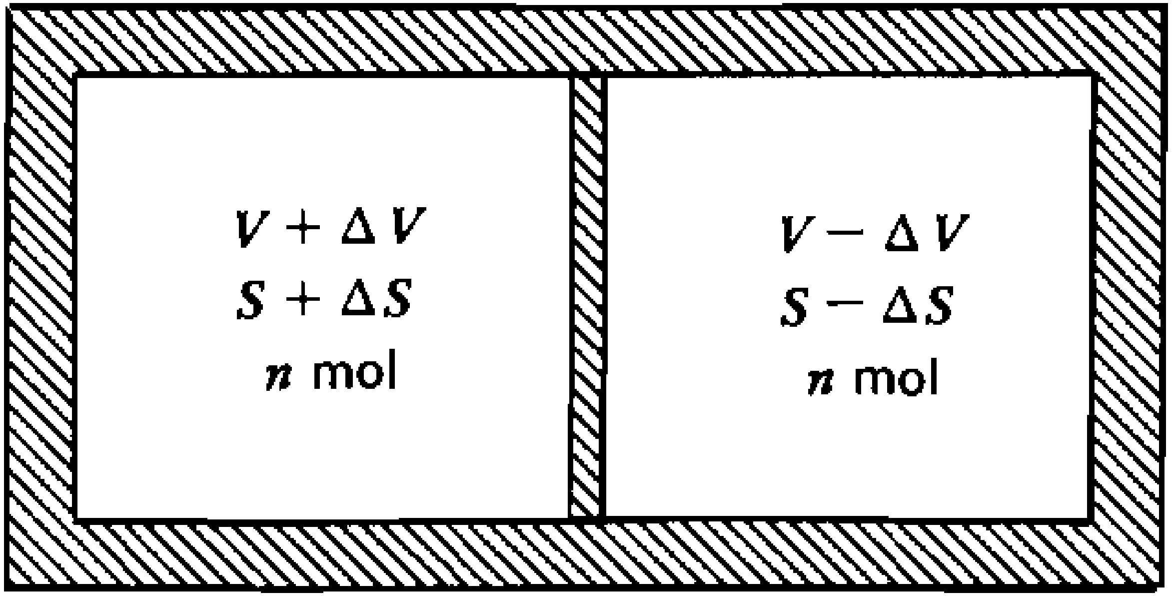

Figure 19.3 A system in a state generated by a virtual variation, for the retained constraints U = constant, V = constant, n = constant. The virtual variation is generated by moving the partition from an initial position in which $\Delta V = 0$ and $\Delta S = 0$ to the position shown.

- If the original state of the system was a stable equilibrium, then the virtual displacement will increase the internal energy and:

  $$U(S+\Delta S, V+\Delta V, n)+U(S-\Delta S, V-\Delta V, n) > 2U(S, V, n)$$

  or

  $$\Delta U > 0$$

  .
- If it is assumed that ΔS and ΔV are small enough that the internal energy may be represented by a Taylor series, then:

  $$U(S+\Delta S, V+\Delta V, n) = U(S, V, n) + \text{Term } 1 + \text{Term } 2$$

- where:

$$\text{Term 1} = \left(\frac{\partial U}{\partial S}\right)_{V,n} (\Delta S) + \left(\frac{\partial U}{\partial V}\right)_{S,n} (\Delta V)$$

and

$$\text{Term 2} = \frac{1}{2}\left[\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,n} (\Delta S)^2 + \left(\frac{\partial^2 U}{\partial V^2}\right)_{S,n} (\Delta V)^2\right]$$

$$+ \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_{V,n}\right)_{S,n} (\Delta V \Delta S)$$

- Therefore:

$$\Delta U = \left(\frac{\partial^2 U}{\partial S^2}\right)_{V,n} (\Delta S)^2 + 2\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_{V,n}\right)_{S,n} (\Delta V \Delta S)$$

$$+ \left(\frac{\partial^2 U}{\partial V^2}\right)_{S,n} (\Delta V)^2 > 0$$

- This is true for all possible values of ΔS and ΔV, if:

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,n} > 0 \text{ and}$$

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,n}\left(\frac{\partial^2 U}{\partial V^2}\right)_{S,n} - \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_{V,n}\right)_{S,n}^2 > 0$$

- It can be shown that:

$$\left(\frac{\partial^2 U}{\partial S^2}\right)_{V,n} = \frac{T}{C_V}$$

$$\left(\frac{\partial^2 U}{\partial V^2}\right)_{S,n} = \frac{C_p}{V\kappa_T C_V}$$

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_{V,n}\right)_{S,n} = -\frac{\alpha T}{\kappa_T C_V}$$

where

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \text{ and } \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

- Note that all of T, V, C_p, C_V, α, and κ_T are positive quantities.
- C_V is positive because of the requirement that $T/C_V > 0$
- Since $C_p > C_V$, $C_p > 0$.
- It may also be shown that:

$$\kappa_T > \frac{\alpha^2 TV}{C_p} > 0$$

.

- These are all stability conditions and are consistent with Le Chatelier's principle: "It is a feature of stable equilibrium that spontaneous processes induced by a deviation from the initial state proceed in such a direction so as to restore the system to the initial state".

The Equilibrium State in a Multicomponent System

- Consider Figure 19.4.
  - This system is similar to Figure 19.1, except that it now includes r subsystems II$_i$ each of which contains only substance i.
  - Each of these are joined to system I by a rigid semipermeable membrane.
    - The semipermeable membranes are specific to substance i and allow for substance i to move between subsystem II$_i$ and subsystem I.
    - There is a pressure difference or p_i across the semipermeable membrane.
    - Heat may not be transferred across the boundary of systems II$_i$ to or from the surroundings.

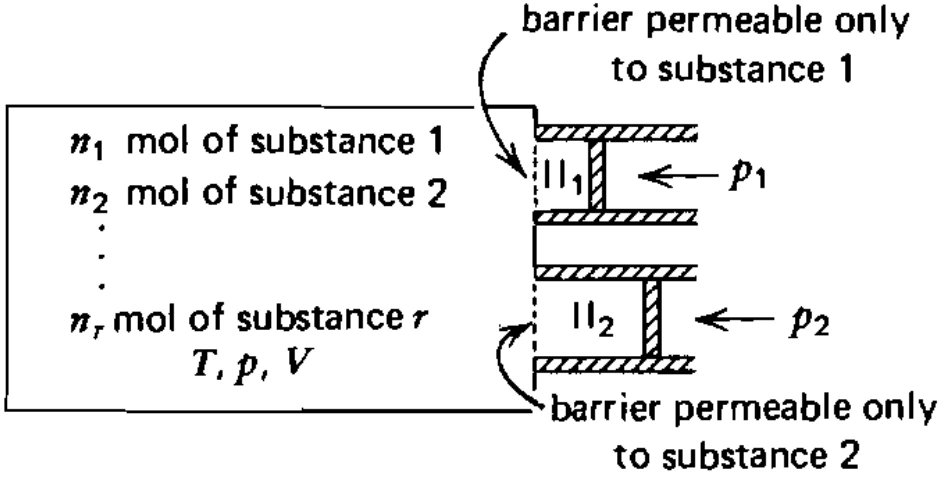

Figure 19.4 Schematic representation of an r-component system with $r + 1$ parts. In part I, which has volume V, are n_1 mol of substance 1, n_2 mol of substance 2, ... , n_r moles of substance r, at T and p. In part II_1 are dn_1 mol of substance 1, at T and whatever pressure p_1 represents equilibrium across the semipermeable membrane. In general, this pressure is different from p. In part II_2 are dn_2 mol of substance 2, at T and whatever pressure p_2 represents equilibrium across the semipermeable membrane. There are r semipermeable membranes, each permitting only one of the components to enter part I; only two are shown in the diagram. The semipermeable membranes define the boundary of part I. Heat may be transferred from the surroundings to part I, but not to parts II_1, II_2, ... , II_r. Also, part I may do work on the surroundings.

- Subsystem I is an r component system containing substances $1, 2, \ldots, r$
  - Subsystem I can transfer heat to and from the surroundings.
  - Subsystem I can do work on the surroundings.
- Substance i in subsystem II$_i$ has molar volume, internal energy, and entropy v_i, u_i, and s_i.
- dn_i moles of i are transferred to part I of the system motion of a piston with pressure p_i.
- System I transfers a corresponding amount of heat dq_i from the surroundings.
- System I increases its volume by $v_i dn_i$ and thus does work $(pdV)_i$ on the surroundings.
- This results in a change in internal energy of the system $dU_i - u_i dn_i = đq_i - (pdV)_i + p_i v_i dn_i$.

- But $h_i \equiv \ u_i + p_i v_i$.
- Therefore:

  $$dU_i = đq_i + h_i dn_i - (pdV)_i$$

  and

  $$dU = TdS - pdV + \sum_{i=1}^{r} \mu_i dn_i$$

  where

  $$\mu_i = h_i - Ts_i$$

  and μ_i is the chemical potential of component i.
- Consider now chemical potential from another perspective:
  - The size of the system is increased by a constant factor ξ.

- The volume of the system is increased from V to ξV.
- The number of moles of each component is changed from n_i to ξn_i
- The entropy of the system is increased from S to ξS.
- Since U is extensive, it is also increased from U to ξU.
- Mathematically this may be written as $U(\xi S, \xi V, \xi n_1, \ldots, \xi n_r) = \xi U(S, V, n_1, \ldots, n_r)$.
- Consider the derivative of this with respect to ξ:

$$\left[\frac{\partial U}{\partial(\xi S)}\right]_{V,n_i} \frac{\partial(\xi S)}{\partial \xi} + \left[\frac{\partial U}{\partial(\xi V)}\right]_{S,n_i} \frac{\partial(\xi V)}{\partial \xi}$$

$$+ \sum_{j=1}^{r} \left[\frac{\partial U}{\partial(\xi n_j)}\right]_{V,S,n_{i\neq j}} \frac{\partial(\xi n_j)}{\partial \xi} = U$$

- This gives:

$$\left[\frac{\partial U}{\partial(\xi S)}\right]_{V,n_i} S + \left[\frac{\partial U}{\partial(\xi V)}\right]_{S,n_i} V + \sum_{j=1}^{r} \left[\frac{\partial U}{\partial(\xi n_j)}\right]_{V,S,n_{i\neq j}} n_j = U$$

- Since there is no restriction on the value of ξ, then the above is true for $\xi = 1$, and:

$$\left[\frac{\partial U}{\partial S}\right]_{V,n_i} S + \left[\frac{\partial U}{\partial V}\right]_{S,n_i} V + \sum_{j=1}^{r} \left[\frac{\partial U}{\partial n_j}\right]_{V,S,n_{i\neq j}} n_j = U$$

- But previously, it has been shown that:

$$\left[\frac{\partial U}{\partial S}\right]_{V,n_i} = T \text{ and } \left[\frac{\partial U}{\partial V}\right]_{S,n_i} = -p$$

- Therefore:

$$TS - pV + \sum_{j=1}^{r} \mu_j n_j = U$$

  if

$$\mu_j \equiv \left[\frac{\partial U}{\partial n_j}\right]_{V,S,n_{i\neq j}}$$

  and μ_j is the chemical potential of component j.

- Similarly

$$H = U + pV = TS + \sum_{j=1}^{r} \mu_j n_j$$

$$A = U - TS = -pV + \sum_{j=1}^{r} \mu_j n_j$$

- and

$$G = U - TS + pV = \sum_{j=1}^{r} \mu_j n_j$$

- The total differential of U may be written as:

$$dU = TdS + SdT - pdV - Vdp + \sum_{j=1}^{r} \mu_j dn_j + \sum_{j=1}^{r} n_j d\mu_j$$

- But:

$$dU = TdS - pdV + \sum_{j=1}^{r} \mu_j dn_j$$

- Therefore:

$$SdT - Vdp + \sum_{j=1}^{r} n_j d\mu_j = 0$$

- This is known as the Gibbs-Duhem equation.
- For a one component system: $G = n\mu$ or

$$g = h - Ts = \frac{G}{n} = \mu$$

- The Legendre transforms of U become:

$$dH = TdS + Vdp + \sum_{j=1}^{r} \mu_j dn_j$$

$$dA = -Sdt - pdV + \sum_{j=1}^{r} \mu_j dn_j$$

$$dG = -Sdt + Vdp + \sum_{j=1}^{r} \mu_j dn_j$$

- But differentiation of

$$G = \sum_{j=1}^{r} n_j \mu_j$$

yields:

$$dG = \sum_{j=1}^{r} n_j d\mu_j + \sum_{j=1}^{r} \mu_j dn_j$$

- The first term may be written as:

$$\sum_{j=1}^{r} n_j d\mu_j = \sum_{j=1}^{r} n_j \left[\left(\frac{\partial \mu_j}{\partial T} \right)_{p,n_j} dT + \left(\frac{\partial \mu_j}{\partial p} \right)_{T,n_j} dp \right]$$

- This is now compared with the Gibbs-Duhem equation.

- It follows that:

$$-S = \sum_{j=1}^{r} n_j \left(\frac{\partial \mu_j}{\partial T}\right)_{p,n_j} = -\sum_{j=1}^{r} n_j \overline{s}_j$$

and

$$V = \sum_{j=1}^{r} n_j \left(\frac{\partial \mu_j}{\partial p}\right)_{T,n_j} = \sum_{j=1}^{r} n_j \overline{v}_j$$

- $\overline{s}_j$ is the partial molar entropy.
- $\overline{v}_j$ is the partial molar volume.
- It may also be shown that:

$$\mu_j = \left[\frac{\partial H}{\partial n_j}\right]_{p,S,n_{i\neq j}} = \left[\frac{\partial A}{\partial n_j}\right]_{V,T,n_{i\neq j}} = \left[\frac{\partial G}{\partial n_j}\right]_{p,T,n_{i\neq j}}$$

- Recall that $G = H - TS$. Therefore:

$$\mu_j = \left[\frac{\partial}{\partial n_j}(H - TS)\right]_{T,p,n_{i \neq j}} = \overline{h}_j - T\overline{s}_j$$

- Now the properties of a multicomponent system at equilibrium may be considered.
- If the composition of the system at all points remains constant, then the previously considered conditions for one-component system applies.
- If the composition varies at constant T and p, it follows from the Gibbs-Duhem equation that:

$$\left(\sum_{j=1}^{r} n_j d\mu_j\right)_{T,p} = 0$$

- For a two component system:

$$n_1 \left(\frac{\partial \mu_1}{\partial n_1}\right)_{T,p,n_2} = -n_2 \left(\frac{\partial \mu_2}{\partial n_1}\right)_{T,p,n_2}$$

  and the chemical potential of one component changes at the expense of the other and total chemical potential is conserved.
- Consider Figure 19.5.
- A virtual variation is constructed for a two component system under the constraint of constant T and p.
  - Initially the system consists of $2n_1$ moles of substance 1 and $2n_2$ moles of substance 2.
  - A barrier is inserted that divides the container into two subsystems each containing n_1 moles of 1 and n_2 moles of 2.

possible coupled variations of the intensive variables T, p, μ_i in a fluid system. Thus, at constant temperature and pressure, any change in the composition of a system leads to changes in the chemical potentials such that

$$\left(\sum_{i=1}^{r} n_i\, d\mu_i\right)_{T,p} = 0. \qquad (19.81)$$

In a two-component system, addition of dn_1 mol of component 1 requires that

$$n_1\left(\frac{\partial \mu_1}{\partial n_1}\right)_{T,p,n_2} = -n_2\left(\frac{\partial \mu_2}{\partial n_1}\right)_{T,p,n_2}. \qquad (19.82)$$

Since n_1 and n_2 are positive, the signs of $(\partial\mu_1/\partial n_1)_{T,p,n_2}$ and $(\partial\mu_2/\partial n_1)_{T,p,n_2}$ must be opposite. The extension to an r-component system is straightforward. To determine the sign of $(\partial\mu_1/\partial n_1)_{T,p,n_2}$ we construct a virtual variation for a two-component system defined to be at equilibrium at some T and p. Let the system consist of a deformable container filled with a mixture of $2n_1$ mol of 1 and $2n_2$ mol of 2 (see Fig. 19.5). Imagine that a semipermeable barrier (passing 1 but not 2) is inserted, dividing the container so that there are n_1 mol of 1 and n_2 mol of 2 on each side. Now let the barrier be displaced from the position in which it was inserted. In this displacement component 1 flows freely through the barrier, but however much of component 2 was on each side of the barrier remains there. We assume that during the displacement the temperature and pressure are maintained constant by exchange of heat and work with the surroundings. After the semipermeable barrier is displaced through some distance, an impermeable barrier is slipped in alongside it, and the combined barriers are displaced back to a position dividing the volume equally. In this second displacement the composition of the mixture on each side of the barrier remains fixed. Again we assume that T and p are maintained constant by exchange of heat and work with the surroundings. As a result of the operations described, we have generated a virtual variation in which, although T and p are the same, the composition of the mixture is different on the two sides of the barrier. Because the original state was one of stable equilibrium, in the virtual variation described it is necessary that

$$\Delta G > 0. \qquad (19.83)$$

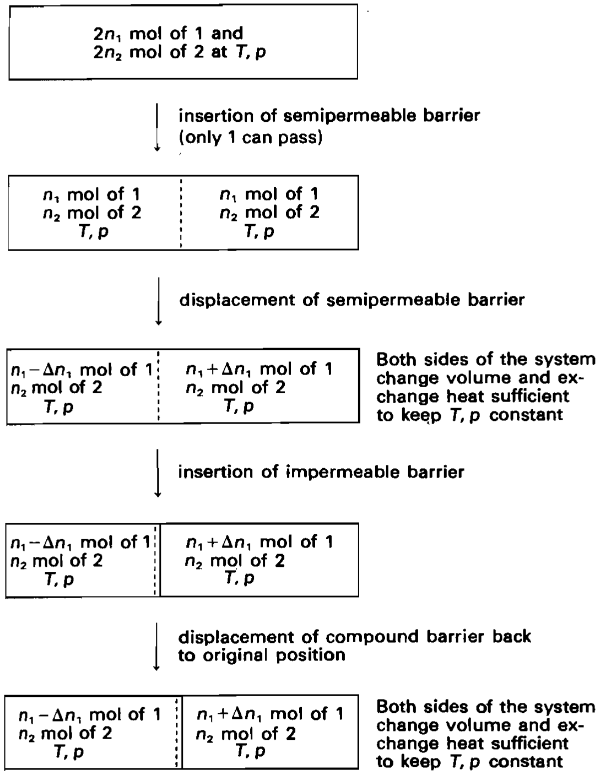

Figure 19.5 A virtual variation at constant T and p that generates a state with a composition difference from an originally homogeneous mixture.

- This barrier is a semipermeable membrane that allows 1 through it, but not 2.
- This barrier is now displaced.
  - Temperature and pressure are maintained at constant values by heat and work crossing the boundary of the system.
- Δn_1 passes through the barrier from one side to the other.
- An impermeable barrier is placed alongside the semipermeable barrier.
- The combined barriers are returned to the original position.
  - Again, temperature and pressure are maintained at constant values by heat and work crossing the boundary of the system.

- As a result of this virtual variation, T and p are constant, but the composition is now different on each side of the barrier.
- Since the original system was at equilibrium, the virtual variation has caused $\Delta G > 0$.

$$\Delta G \equiv \; G(T,p,n_1+\Delta n_1,n_2)+G(T,p,n_1-\Delta n_1,n_2)$$

$$-2G(T,p,n_1,n_2) > 0$$

- If Δn_1 is small, a Taylor series expansion may be used and truncated after the second order term.
  - Since the expansion is about the equilibrium position, the first order term vanishes and:

$$\Delta G = \left(\frac{\partial^2 G}{\partial n_1^2}\right)_{T,p,n_2} > 0$$

- Since $\mu_1 = (\partial G/\partial n_1)_{T,p,n_2}$, this means that:

$$\left(\frac{\partial \mu_1}{\partial n_1}\right)_{T,p,n_2} > 0$$

- Since total chemical potential is conserved:

$$\left(\frac{\partial \mu_2}{\partial n_1}\right)_{T,p,n_2} < 0$$

- The addition of component i at constant T, p, and n_j of other components increases the chemical potential of component i.
- Consider the behaviour of $n_2\,(\partial \mu_i/\partial n_1)_{T,p,n_2}$ as n_1 becomes small.

- Small ratios of n_1/n_2 are consistent with nearly pure 2.
- In this limiting case, $n_2\left(\partial\mu_2/\partial n_1\right)_{T,p,n_2}$ approaches a constant negative, nonzero value:

$$\lim_{n_1\to 0} n_2\left(\frac{\partial\mu_2}{\partial n_1}\right)_{T,p,n_2} = -B$$

- This means that:

$$\lim_{n_1\to 0} n_1\left(\frac{\partial\mu_1}{\partial n_1}\right)_{T,p,n_2} = B$$

and

$$\left(\frac{\partial\mu_2}{\partial n_1}\right)_{T,p,n_2} = -\frac{B}{n_2} = -\frac{n_1}{n_2}\left(\frac{\partial\mu_1}{\partial n_1}\right)_{T,p,n_2}$$

- This may be rewritten as:

$$\left(\frac{\partial \mu_1}{\partial n_1}\right)_{T,p,n_2} = \frac{B}{n_1}$$

- This may be integrated to:

$$\mu_1 = B \ln n_1 + f(T, p, n_2)$$

  where $f(T, p, n_2)$ is an arbitrary function.

- Since chemical potential is an intensive function, it cannot depend on the value of n_1, but on the ratio n_1/n_2.
- Therefore the above may be rewritten as:

$$\mu_1 = B \ln \frac{n_1}{n_1 + n_2} + \mu_1^0(T, p)$$

- μ_1^0 is the chemical potential of the pure substance.
- B must have units of energy per mole and will later be shown to be RT.
- Chemical equilibrium will now be considered in terms of chemical potential.
- Recall that:

  $$\sum_{i=1}^{r} \nu_i X_i = 0$$

  where ν_i is the stoichiometric coefficient (and is negative for reactants and positive for products) and X_i is one mole of component i.
- Through conservation of mass, changes in n_i, the amount of component i are related.

- Thus:

$$\frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2} = \ldots = \frac{dn_r}{\nu_r} = d\lambda$$

  where λ is the progress variable and is relative to some arbitrary reference point.
- When $d\lambda/dt = 0$, no reaction is in progress.
- λ may be used to describe the equilibrium composition after a reaction is complete.
- Consider a closed homogeneous system with constraints of constant entropy and volume:

$$(dU)_{S,V} = \sum_{i=1}^{r} \mu_i dn_i = \sum_{i=1}^{r} \nu_i \mu_i d\lambda$$

- If this system is at equilibrium, then λ_{equil} would correspond to $(dU)_{S,V}$ =0 and a displacement from equilibrium by $\Delta\lambda = \lambda - \lambda_{equil}$ gives:

$$\left[\left(\sum_{i=1}^{r} \nu_i \mu_i\right) \Delta\lambda\right]_{S,V} > 0.$$

- If $\Delta\lambda > 0$ then:

$$\left(\sum_{i=1}^{r} \nu_i \mu_i\right) > 0$$

- If $\Delta\lambda < 0$ then:

$$\left(\sum_{i=1}^{r} \nu_i \mu_i\right) < 0$$

- At equilibrium:$\left(\sum_{i=1}^{r} \nu_i \mu_i\right) = 0$

- Chemical potential may be generalized to a mixture with r components:

$$\mu_1 = B \ln \frac{n_1}{n_1 + \cdots + n_r} + \mu_1^0(T, p)$$

where:

$$x_1 = \frac{n_1}{n_1 + \cdots + n_r}$$

the mole fraction of component i.

- Therefore the condition for equilibrium becomes:

$$\sum_{i=1}^{r} \nu_i [B \ln x_i + \mu_i^0(T, p)] = 0$$

- This may be rewritten as:

$$-\frac{1}{B}\sum_{i=1}^{r}\nu_i\mu_i^0(T,p)=\sum_{i=1}^{r}\ln x_i^{\nu_i}$$

- The right hand side of the equation is recognized as:

$$\ln K(T,p)=\sum_{i=1}^{r}\ln x_i^{\nu_i}$$

  where $K(T,p)$ is the equilibrium coefficient.
- If $B=RT$ then:

$$\sum_{i=1}^{r}\nu_i\mu_i^0(T,p)=\Delta G_{reac}=-RT\ln K(T,p)$$

- It is important to note that this derivation is based on the basis that n_1/n_2 was small.
  - What if it is not small?

The Properties of Pure Gases and Gas Mixtures

- Chapter 21 will be revisited to address the following:
  - How may observations of the properties of a gas be translated into values of thermodynamic functions that represent the state of the gas?
  - What is the detailed relationship between the structure of the molecules that compose the gas and the thermodynamic properties of the gas?
  - How do molecular interactions influence the thermodynamic properties of the gas?
  - Which aspects of molecular structure and molecular interactions influence chemical equilibrium?

Thermodynamic Description of a Pure Gas

- The perfect gas obeys the equation of state:

$$p = \frac{nRT}{V}$$

- It served to describe gases at atmospheric pressures and contributed to the development of key concepts in chemistry and thermodynamics:
  - The provided the first method of establishing relative molar masses.
  - It provided a temperature scale that was also a thermodynamic temperature scale.
  - It provided a moderately accurate representation of behaviour of the properties of real gases near 1 atm.
  - It describes the limiting behaviour of real gases in the limit of low pressure.

- Properties of real substances in the gas phase are:
  - At sufficiently low pressure, all gases satisfy the perfect gas equation of state.
  - At sufficiently low temperature and high pressure, all gases condense to either a solid or liquid phase.
    - There is a range of temperature and pressure where liquid and gas coexist in equilibrium.
    - There is a range of temperature and pressure where liquid and solid coexist in equilibrium.
    - There is one point where gas, liquid, and solid coexist (the triple point).
  - For each substance, there exists a critical temperature.
    - Above the critical temperature, it is impossible to condense a gas to liquid no matter how high the pressure.

- Continued:
  - At the critical temperature T_c , the difference in density between the liquid and the gas vanish.
  - At this point, the density and pressure are referred to as the critical density n/V_c and critical pressure p_c.
- The properties of many real gases may be represented reasonably well by one equation of state if the temperature, pressure, and volume are scaled by their values at the critical point.
  - These are referred to as the reduced temperature, pressure and volume.

$$\tilde{T} \equiv \frac{T}{T_c}, \tilde{V} \equiv \frac{V}{V_c}, \text{and } \tilde{p} \equiv \frac{p}{p_c}$$

  - This is the principle of corresponding states.

- The thermodynamic description of a gas relates the equation of state to changes in thermodynamic potential:

$$\Delta U = U(T_2, V_2) - U(T_1, V_1)$$

$$= \int_{T_1,V_1}^{T_2,V_1} C_V(T, V_1) dT + \int_{T_2,V_1}^{T_2,V_2} \left[T_2 \left(\frac{\partial p}{\partial T} \right)_V - p \right] dV$$

$$\Delta H = H(T_2, p_2) - H(T_1, p_1)$$

$$= \int_{T_1,p_1}^{T_2,p_1} C_p(T, p_1) dT + \int_{T_2,p_1}^{T_2,p_2} \left[V - T_2 \left(\frac{\partial V}{\partial T} \right)_p \right] dp$$

$$\Delta S = S(T_2, p_2) - S(T_1, p_1)$$

$$= \int_{T_1,p_1}^{T_2,p_1} \frac{C_p(T, p_1)}{T} dT + \int_{T_2,p_1}^{T_2,p_2} \left(\frac{\partial V}{\partial T} \right)_p dp$$

- Recall that in the limit of low pressure,

$$\lim_{p\to 0} \frac{pV}{nRT} = 1$$

- As illustrated in Figure 21.1, different real gases approach this limit at different rates.
- The thermodynamic properties of a real gas are influenced by two factors.
  - The internal structure of the gas determines the moments of inertia and vibrational, rotational, and electronic spectra. This in turn influences the heat capacity.
  - The interactions between and among molecules influence the deviations from the ideal equation of state.

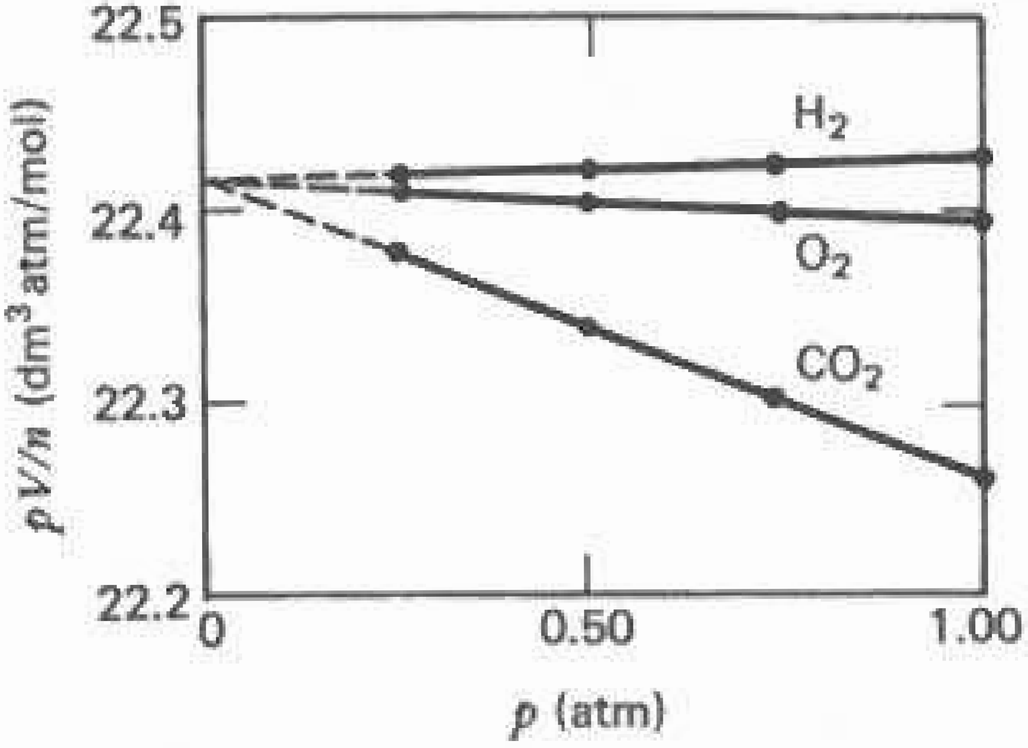

Figure 21.1 The pV product for three gases, showing the universal approach to the ideal gas value as the pressure tends to zero. From R. H. Cole and J. S. Coles, *Physical Principles of Chemistry* (Freeman, San Francisco, 1964).

- Heat capacities of real gases may be considered in terms of their deviation from that of a perfect gas.
- As pressure approaches zero, C_p^* becomes a function only of temperature.
    - Because internal degrees of freedom matter, there are different limiting values of $C_p^*(T)$ for different gases (See Table 21.1)
- Similarly $C_V^*(T)$, $U^*(T)$, and $H^*(T)$ are the low pressure limits of the heat capacity at constant volume, internal energy, and enthalpy, respectively.
- Since:

$$C_p^*(T) = \lim_{p \to 0} \left(\frac{\partial H}{\partial T} \right)_p = \frac{dH^*}{dT}$$

$$C_v^*(T) = \lim_{p\to 0} \left(\frac{\partial U}{\partial T}\right)_V = \frac{dU^*}{dT}$$

and

$$H^* = U^* + \lim_{p\to 0} pV$$

$$= U^* + nRT$$

it follows that

$$C_p^*(T) = C_v^*(T) + nR$$

- Thus $C_p^*(T)$ and $C_V^*(T)$ may be considered the contributions to the heat capacity that depend only on the internal structure of the molecules and not on their interactions.
- It is now possible to consider a gas at some pressure T_2, p_2, V_2 relative to an arbitrary T_1, p_1, V_1.

- Choose $T_1 = T_2$, $p_1 = 0$, and $V_1 = \infty$.
- Therefore:

$$U(T_2, V_2) = U^*(T_2) + \int_{T_2,\infty}^{T_2,V_2} \left[T_2 \left(\frac{\partial p}{\partial T} \right)_V - p \right] dV$$

$$H(T_2, p_2) = H^*(T_2) + \int_{T_2,0}^{T_2,p_2} \left[V - T_2 \left(\frac{\partial V}{\partial T} \right)_p \right] dp$$

- Now consider the equation for entropy which includes the term:

$$\int_{T_2,p_1}^{T_2,p_2} \left(\frac{\partial V}{\partial T} \right)_p dp$$

- For a perfect gas:

$$\int_{T_2,p_1}^{T_2,p_2} \left(\frac{\partial V}{\partial T}\right)_p dp = \int_{T_2,p_1}^{T_2,p_2} \frac{nR}{p} dp$$

  which diverges in the limit of $p \to 0$.

- For a real gas:

$$\lim_{p\to 0}\left[\left(\frac{\partial V}{\partial T}\right)_P - \frac{nR}{p}\right] = f(T)$$

  where $f(T)$ is observed to be finite and bounded at all pressures.

  - This means that the difference in behaviour of a real and an ideal gas is a finite and bounded quantity.

- $S(T_2, p_2)$ may be rewritten as:

$$S(T_2, p_2) = S(T_1, p_1) + \int_{T_2, p_1}^{T_2, p_2} \frac{C_p(T, p_1)}{T} dT$$

$$- \int_{T_2, p_1}^{T_2, p_2} \left[\left(\frac{\partial V}{\partial T} \right)_P - \frac{nR}{p} \right] dp - \int_{T_2, p_1}^{T_2, p_2} \frac{nR}{p} dp$$

- Let p be a reference pressure based on the unit in which pressure is expressed.
- Then, when $p_1 \rightarrow 0$,

$$S(T_2, p_2) = S^*(T_2, \mathcal{P}) + \int_{T_2, 0}^{T_2, p_2} \left[\frac{nR}{p} - \left(\frac{\partial V}{\partial T} \right)_p \right] dp - nR \ln \frac{p_2}{\mathcal{P}}$$

where $\int_{p_1}^{p_2} (nR/p) dp$ has been subtracted from both S and S^*.

- $S^*(T_2, \mathcal{P})$ is the entropy of a perfect gas at (T_2, p):

$$S^*(T_2, \mathcal{P}) = \int_{T_{ref}^{T_2|}} \frac{C_p^*(T)}{T} dT + S_0^*(T_{ref}, \mathcal{P})$$

- The value of $S_0^*(T_{ref}, \mathcal{P})$ is determined by the lower limit of integration.
- $p/\mathcal{P}$ is dimensionless and $\mathcal{P}$ is required for this purpose.
- Entropy of a perfect gas depends on pressure.
- This suggests a functional form for a property of a gas known as fugacity, f:

$$f = p \exp\left[\frac{1}{RT}\int_0^p \left(v - \frac{RT}{p'}\right) dp'\right]$$

- Fugacity has units of pressure.
- The exponential portion of the expression contains all the information about the non-perfect behaviour of the gas.
- As $p \rightarrow 0,\ f \rightarrow p$.
- Fugacity is convenient for the consideration of the chemical potential of a real gas.
- For a real gas:

$$\mu(T,p) \equiv \frac{G}{n} \equiv \frac{H - TS}{n}$$

$$= h^*(T_{ref}) - T s_0^*(T_{ref}, \mathcal{P}) + RT \ln \frac{p}{\mathcal{P}}$$

$$+ \int_{T_{ref}}^{T} \left(1 - \frac{T}{T'}\right) C_p^*(T') dT' + \int_{0,T}^{p,T} \left(v(p') - \frac{RT}{p'}\right) dp'$$

- Continued:

$$\mu(T,p) = \mu^*(T,\mathcal{P}) + RT\ln\frac{p}{\mathcal{P}} + \int_{0,T}^{p,T}\left(v(p') - \frac{RT}{p'}\right)dp'$$

$$= \mu^*(T,\mathcal{P}) + RT\ln\frac{f}{\mathcal{P}}$$

  where $\mu^*(T,\mathcal{P})$ is the chemical potential of a perfect gas at $(T,\mathcal{P})$.
- For a perfect gas this is:

$$\mu(T,p) = \mu^*(T,\mathcal{P}) + RT\ln\frac{p}{\mathcal{P}}$$

- Fugacity plays a role similar to pressure in thermodynamics.
  - In mixtures, it is possible to have partial fugacities.

Thermodynamic Description of a Gas Mixture

- To describe the properties of a mixture, it is necessary to specify the temperature, pressure, total volume, and the composition.
- Any unit may be used, but mole fraction is often convenient.

$$x_i = \frac{n_i}{n_1 + n_2 + \cdots + n_r}$$

- Mole fraction is related to partial pressure:

$$\lim_{p \to 0} \frac{p_i}{p} = x_1$$

or:

$$\lim_{p \to 0} p = \frac{RT}{V}(n_1 + n_2 + \cdots + n_r) = (p_1 + p_2 + \cdots + p_r)$$

- The composition variables are not completely independent of each other.
  - Mole fractions must add up to unity.
  - Partial pressures must add up to the total pressure.
- Equilibria will impose additional constraints on composition.
  - Consider the reaction:

$$H_2 + I_2 \rightleftharpoons 2HI$$

  - Only two of the three concentrations are independent.
  - The third is determined by the equilibrium.
- Consider Figure 21.9 in which a container is separated into two compartments by a semipermeable membrane.

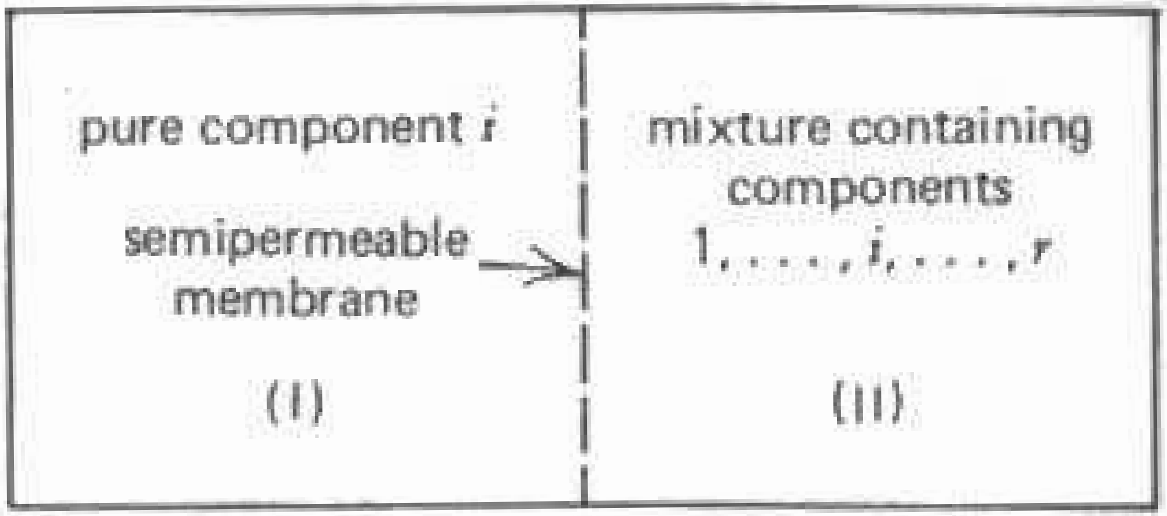

Figure 21.9 Schematic diagram of a box with semipermeable membrane separating pure component i from a mixture of gases containing component i. Only i can pass through the membrane.

- Compartment I contains pure i in equilibrium with with component i in the gas mixture in compartment II.
- The semipermeable membrane is also diathermal and rigid and heat but not work can be transferred from one compartment to the other.
- The system is in equilibrium, so:

$$\mu_i^I = \mu_i^{II} = \mu_i$$

$$T^I = T^{II} = T$$

- For gas mixtures at nonzero pressure:

$$\mu_i^I = \mu_i^*(T, \mathcal{P}) + RT \ln \frac{p^I}{\mathcal{P}} + \int_{0,T}^{p^I,T} \left[\overline{v}_i(p') - \frac{RT}{p'} \right] dp'$$

- For the system in Figure 21.9, $p_i^I = p_i^I I$.
- In the low pressure limit, $p_i^I = p^I = x_i^{II} p^I I$.
- Therefore the chemical potential of i in compartment II is:

$$\mu_i^{II} = \mu_i^*(T, \mathcal{P}) + RT \ln \frac{x_i^{II} p^{II}}{\mathcal{P}} + \int_{0,T}^{p^{II},T} \left[\overline{v}_i(p') - \frac{RT}{p'} \right] dp'$$

where:

$$\overline{v}_i = \left(\frac{\partial \mu_i}{\partial p} \right)_{T,n_j} = \frac{\partial}{\partial p} \left(\frac{\partial G}{\partial n_i} \right)_{T,n_{j\neq i}} = \frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial p} \right)_{T,n_{j\neq i}}$$

$$= \left(\frac{\partial V}{\partial n_i} \right)_{T,p,n_{i\neq j}}$$

- Chemical potential may be determined from the equation of state for the substance.
- The average molar volume for the mixture may be considered in terms of the virial equation of state:

$$v_m = \frac{V}{\sum_{i=1}^{r} n_i} = \frac{RT}{p} + B(x_1, x_2, \cdots, x_{r-1}, T)$$

  where B is an extension of the virial equation to account for interaction of molecules and is proportional to the frequency of occurence of all possible pairs.
- Thus:

$$B(x_1, x_2, \cdots, x_{r-1}, T) = \sum_{i=1}^{r} \sum_{j=1}^{r} x_i x_j B_{ij}(T)$$

- By symmetry, $B_{ij} = B_{ji}$.
- For a binary mixture:

$$\frac{V}{n_1 + n_2} = \frac{RT}{P} + \frac{n_1^2 B_{11} + 2n_1 n_2 B_{12} + n_2^2 B_{22}}{(n_1 + n_2)^2}$$

- But:

$$\overline{v}_1 = \left(\frac{\partial V}{\partial n_1} \right)_{T,p,n_2}$$

- Therefore:

$$\overline{v}_1 = \frac{RT}{p} + \frac{n_1^2 B_{11} + 2n_1 n_2 B_{11} + 2n_2^2 B_{12} - n_2^2 B_{22}}{(n_1 + n_2)^2}$$

- This may be rewritten as:

$$\overline{v}_1 = \frac{RT}{P} + x_1^2(2B_{11} - B_{11}) + x_1x_2(2B_{11} - B_{12})$$

$$+x_2x_1(2B_{12} - B_{21}) + x_2^2(2B_{12} - B_{22})$$

- Generally:

$$\overline{v}_i = \frac{RT}{P} + \sum_{j=1}^{r}\sum_{k=1}^{r} x_jx_k(2B_{ij} - B_{jk})$$

- Therefore:

$$\mu_i = \mu_i^*(T) + RT\ln\frac{px_i}{\mathcal{P}} + \sum_{j=1}^{r}\sum_{k=1}^{r} x_jx_k(2B_{ij} - B_{jk})p$$

- For a pure gas:

$$\mu_i = \mu_i^*(T) + RT \ln \frac{p}{\mathcal{P}} + B_{11} p$$

- In a mixture of real gases, interactions between molecules of 1 and 2 are not expected to be the same as interactions between molecules of 1 with 1 or molecules of 2 with 2.
- Yet it is desirable to make predictions about properties of gas mixtures and relate these properties to the properties of the pure components.
- Fugacity of component i in a mixture has been defined by Lewis and Randall as:

$$f_i = x_i p \exp\left[\int_0^p \left(\overline{v}_i - \frac{RT}{p'}\right) \frac{dp'}{RT}\right]$$

- This gives a partial fugacity:

$$f_i(T,p,x_i) = x_i f_i^0(T,p)$$

  where f_i^0 is the fugacity of pure component i.

  - If this is valid for a mixture, then that mixture is an ideal solution.

- The chemical potential in terms of fugacity is:

$$\mu_i^0 = \mu_i^*(T,\mathcal{P}) + RT\ln\frac{f_i^0}{\mathcal{P}}$$

  for a pure gas and

$$\mu_i = \mu_i^*(T,\mathcal{P}) + RT\ln\frac{f_i}{\mathcal{P}}$$

  for a gas mixture.

- Substituting the pure gas expression into the expression for gas mixtures yields:

$$\mu_i = \mu_i^0 + RT \ln \frac{f_i}{f_I^0}$$

- Thus for an ideal solution:

$$\mu_i = \mu_i^0 + RT \ln x_i$$

- For an equation of state that follows the virial form, it may be shown that:

$$f_i^0 = p \exp\left(\frac{Bp}{RT}\right)$$

- For a virial equation of state that has been extended to account for attractions between like and unlike molecules:

$$f_i^0 = x_i p_i \exp\left[\frac{\sum_{j=1}^{r}\sum_{k=1}^{r} x_j x_k (2B_{ij} - B_{jk})p}{RT}\right]$$

- As $p \rightarrow 0$, $f_i^0 \rightarrow p_i^0$ and $f_i \rightarrow p_i$.
- When considering a mixture of gases, entropy of mixing must be taken into account.
- The partial molar entropy of a gas is:

$$\overline{s}_i = -\left(\frac{\partial \mu_i}{\partial T}\right)_{p,x_j}$$

- This gives:

$$\overline{s}_i = s_i^*(T,\mathcal{P}) - R\ln\frac{px_i}{\mathcal{P}} - \int_{0,T}^{p,T}\left[\left(\frac{\partial\overline{v}_i}{\partial T}\right)_{p',n_i} - \frac{R}{p'}\right]dp'$$

- For a system of pure gases that are separated:

$$S^0 = \sum_{i=1}^{r} n_i s_i^0$$

- For the same gases mixed:

$$S^m = \sum_{i=1}^{r} n_i \overline{s}_i$$

- The difference is due to the entropy of mixing.

- The entropy of mixing is:

$$\Delta S_{mix} = S^m - S^0 = \sum_{i=1}^{r} n_i(\overline{s}_i - s_i^0)$$

$$= -R\sum_{i=1}^{r} n_i \ln x_i + \sum_{i=1}^{r} n_i \int_{0,T}^{p,T} \left[\left(\frac{\partial v_i}{\partial T}\right)_{p'} - \left(\frac{\partial \overline{v}_i}{\partial T}\right)_{p',n_j}\right] dp'$$

- In the limit of low pressure for an ideal solution:

$$\left(\frac{\partial v_i}{\partial T}\right)_{p'} = \left(\frac{\partial \overline{v}_i}{\partial T}\right)_{p',n_j}$$

and for perfect gases:

$$\Delta S_{mix} = -R\sum_{i=1}^{r} n_i \ln x_i$$

- Consider a container with two compartments in contact with a thermal reservoir (Figure 21.10).
- Pressure and temperature are the same on both sides:

$$n_a = \frac{pV^I}{RT}; \quad n_b = \frac{pV^{II}}{RT}$$

- When the partition is removed, the gases mix.
  - After mixing:

$$p = \frac{RT}{V^I + V^{II}}(n_a + n_b)$$

- Since molecules of a perfect gas in an ideal gas solution behave as if individually present, the gas in each compartment may be considered as expanding into the other.

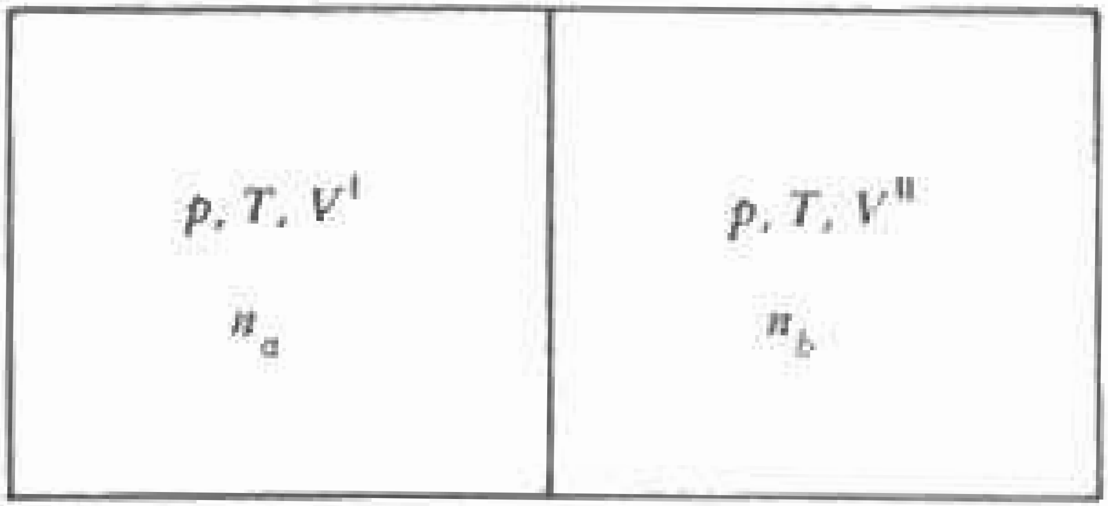

Figure 21.10 Schematic representation of a box separated into two compartments I and II, both at the same temperature and pressure, but containing n_a mol of a and n_b mol of b, respectively.

- The entropy change for a perfect gas undergoing isothermal expansion is:

$$\Delta S = nR\ln\frac{V_2}{V_1}$$

- For each gas expanding into the other compartment:

$$\Delta S_{mix} = \Delta S_1 + \Delta S_2 = n_a R\ln\frac{V^I + V^{II}}{V^I} + n_b R\ln\frac{V^I + V^{II}}{V^{II}}$$

$$= -n_a R\ln\frac{n_a}{n_a + n_b} - n_b R\ln\frac{n_b}{n_a + n_b}$$

$$= -n_a R\ln x_a - n_b R\ln x_b$$

and the spontaneous process has maximized entropy.

- Consider now the inverse process.
- This requires the use of a semipermeable membrane, through which species a can pass, but not species b.
- This membrane is inserted at one end of the container holding the mixture.
- It is then moved and used to compress the gas to an arbitrarily small volume.
    - Species a moves through the barrier, while species b is compressed to the arbitrarily small volume.
    - Recall that for compression:

$$s = -nRT \ln \frac{V_2}{V_1}$$

    - The membrane does work only on species b, not species a.

- At the end of the compression a is in volume $V^I + V^{II}$, while b is in the arbitrarily small volume.
- Next the membrane is replaced with an impermeable piston, which is then moved to the original position of the barrier.
  - The system has been restored to its original state.
- The total work done is:

$$w = -n_b RT \ln \frac{0^+}{V^I + V^{II}} - n_a RT \ln \frac{V^I}{V^I + V^{II}} - n_b RT \ln \frac{V^{II}}{0^+}$$

$$= -\left(n_a RT \ln x_a + n_b RT \ln x_b\right)$$

- But for an isothermal expansion or compression in a perfect gas, $\Delta U = 0$.

- From the first law of thermodynamics, it follows:

$$T\int dS = \int pdV = -w_{sep'n}$$

  and the entropy change due to separation is:

$$\Delta S_{sep'n} = n_a R \ln x_a + n_b R \ln x_b$$

$$\Delta S_{sep'n} = -\Delta S_{mix}$$

- Only molecules with some distinquishing feature may be separated.
  - If the molecules were all the same, they would stay on the same side of the semipermeable membrane and no separation would occur.
  - Dalton's law of partial pressures contains information on the distinquishability of molecules.

- Changes due to mixing are also associated with V, U, H, G, and A.
  - The value of the quantity in a mixture is different that that due to corresponding pure amounts.
  - The difference is the excess value.
- Consider volume:

$$v_E \equiv \frac{V^E}{\sum_{i=1}^{r} n_i} = v_m - \sum_{i=1}^{r} x_i v_i^0$$

- Similarly for enthalpy:

$$h_E \equiv \frac{H^E}{\sum_{i=1}^{r} n_i} = h_m - \sum_{i=1}^{r} x_i h_i^0$$

- We have already established that excess entropy is associated with mixing:

$$s_E \equiv \frac{\Delta S_{mix}}{\sum_{i=1}^{r} n_i}$$

- There are two factors that contribute to an excess function.
  - The first factor is the difference in intermolecular forces between molecules in the mixture and in the pure components.
  - This is what is addressed by the term:

$$\sum_{i=1}^{r} n_i \int_{0,T}^{p,T} \left[\left(\frac{\partial v_i}{\partial T} \right)_{p'} - \left(\frac{\partial \overline{v}_i}{\partial T} \right)_{p',n_j} \right] dp'$$

- This term is zero for a perfect gas and non-zero for gases with intermolecular forces.
- In a perfect gas mixture, the contribution of this term is zero.
- The second factor is due to the distinquishability of different molecular species.
- In entropy, this is addressed by the term:

$$-R\sum_{i=1}^{r} x_i \ln x_i$$

- For any gas mixture, it may be shown:

$$H^E = \int_0^p \left[V^E - T\left(\frac{\partial V^E}{\partial T}\right)_{p',n_j} \right] dp'$$

- For a perfect gas mixture:

$$s_E \equiv \frac{\Delta S_{mix}}{\sum_{i=1}^{r} n_i} = -R\sum_{i=1}^{r} x_i \ln x_i$$

$$h^E = u^E = 0$$

$$v^E = 0$$

$$g_E \equiv \frac{\Delta G_{mix}}{\sum_{i=1}^{r} n_i} = RT\sum_{i=1}^{r} x_i \ln x_i$$

$$a_E \equiv \frac{\Delta A_{mix}}{\sum_{i=1}^{r} n_i} = RT\sum_{i=1}^{r} x_i \ln x_i$$

- For an ideal solution, it may be shown that:

$$\Delta S_{mix} = \sum_{1=i}^{r} n_i \left[\left(\frac{\partial \mu_i^0}{\partial T} \right)_P - \left(\frac{\partial \mu_i}{\partial T} \right)_{p,n_j} \right] = -R \sum_{i=1}^{r} n_i \ln x_i$$

Thermodynamic Description of Gaseous Reactions

- For mixture of gases that reaches equilibrium, it is necessary that:

$$\sum_{i=1}^{r} \nu_i \mu_i = 0$$

- Recall that:

$$\mu_i = \mu_i^*(T, \mathcal{P}) + RT \ln \frac{x_i p}{\mathcal{P}} + \int_{0,T}^{p,T} \left[\overline{v}_i(p') - \frac{RT}{p'} \right] dp'$$

- Therefore, at equilibrium:

$$\sum_{i=1}^{r} \nu_i \mu_i^*(T,\mathcal{P}) = -RT \sum_{i=1}^{r} \left[\ln \frac{x_i p}{\mathcal{P}} + \int_{0,T}^{p,T} \left(\overline{v}_i - \frac{RT}{p'} \right) \frac{dp'}{RT} \right] \nu_i$$

- Since the left-hand side of this equation is a function only of temperature, this means that specifying the temperature will fix the composition.
- The equilibrium coefficient $K(T)$ is defined by:

$$-RT \ln K(T) \equiv \sum_{i=1}^{r} \nu_i \mu_i^*(T,\mathcal{P})$$

- This becomes:

$$K(T) = \prod_{i=1}^{r} \left(\frac{f_i}{\mathcal{P}} \right)^{\nu_i}$$

- In the perfect gas limit, $f_i \rightarrow px_i$, therefore the equilibrium coefficient in terms of partial pressures is:

$$K_p \equiv \prod_{i=1}^{r} \left(\frac{x_i p}{\mathcal{P}} \right)^{\nu_i}$$

- In the limit of low pressure:

$$\lim_{p \rightarrow 0} K_p = K(T)$$

- It can be shown:

$$\sum_{i=1}^{r} \nu_i \mu_i^* = \Delta G^*(T, \mathcal{P})$$

- Therefore: $-RT \ln K(T) = \Delta G^*(T, \mathcal{P})$

- ΔG^* is the difference in molar free energy of reactants and products and depends only on temperature.
- This is in constrast to K_p which does depend on pressure.
- The temperature dependence of $K(T)$ may be elucidated as follows:

$$-R\frac{d\ln K}{dT} = \frac{d}{dT}\left(\frac{\Delta G^*}{T}\right) = -\frac{\Delta G^*}{T^2} + \frac{1}{T}\frac{d\Delta G^*}{dT}$$

  - Since G^* is a state function:

$$\frac{d\Delta G^*}{dT} = \Delta\left(\frac{dG^*}{dT}\right) = -\Delta S^*$$

- Therefore:

$$-R\frac{d\ln K}{dT} = -\frac{1}{T}\left(\frac{\Delta G^*}{T} + \Delta S\right) = -\frac{\Delta H^*}{T^2}$$

- It may also be shown that:

$$\Delta S^* = R\frac{d}{dT}(T\ln K) = \frac{\Delta H^* - \Delta G^*}{T}$$

  - As $K(T)$ increases, ΔS^* increases.
  - The extent that a reaction proceeds when it reaches equilibrium is determined by thermodynamics through the balance of the enthalpy change required and T times the entropy change associated with the reaction.

- If ΔS^* is the same, an exothermic reaction will go more to completion than an endothermic reaction.
- If ΔH^* is the same, then the equilibrium position favours the side of the reaction that has the most molecules.
  - If a reaction has more molecules of products than molecules of reactants, production of products will be thermodynamically favoured.
  - If a reaction has more molecules of reactants than molecules of products, then the production of products is thermodynamically unfavoured.
- ΔH^* and ΔS^* are defined with respect to the reactants and products in their hypothetically perfect gas in a reference state.
  - The reference state what is most widely used is 1 atm pressure and a temperature of 25°C.

- This has been superseded by a standard pressure of 1 bar.
- In a nonideal mixture, the equilibrium coefficient $K(T, p)$ has a slight dependence on pressure since there is a nonzero excess volume.
    - When the reference state is the hypothetical perfect gas, the equilibrium coefficient is independent of pressure.
    - This means that it is possible to calculate equilibrium coefficient and its temperature dependence from tabulated standard thermodynamic enthalpies, entropies, and Gibbs free energies.
    - If the reaction of interest is not tabulated, then Hess's law may be used to construct it from known reactions.

- In most cases, corrections for the fact that gases are not perfect are not necessary.
- There are a number of approximations that correct equilibrium coefficients for the effect of interactions among molecules.
  - For example, Lewis and Randall introduced an approximation based on:

$$B_{jk} = \frac{1}{2}(B_{jj} + B_{kk})$$

    - Note that this contradicts molecular theory which shows that molecular interactions among different possible pairs of molecules are all different, ie. B_{jj}, B_{kk}, and B_{jk} are all different.

- From this it may be shown that:

  $$\ln \frac{K_p}{K(T)} = -p\frac{\Delta B}{RT}$$

  where $\Delta B = \sum_{i=1}^{r} \nu_i B_{ii}(T)$.
- Although this does not have a solid physical basis, it does reasonably well at high pressures.
- It is convenient because it does not require knowledge of the thermodynamic properties of the mixture, but just properties of the pure components.
- If $\Delta B < 0$, this predicts that $K_p/K(T)$ is greater than unity and increases as p increases, resulting in a higher yield of products than is predicted by assuming perfect gases.

Thermodynamic Properties of Solids

- There are a number of important differences between gas and liquid phases.
  - In condensed phases N/V, the number density of molecules, is comparable to the closest packing density of the molecules.
  - This means that interactions between molecules are significant and that there are more than pairwise interactions involved.
  - The translational energy of the molecules is, on average, less than or approximately equal to the height of the potential energy barriers separating the equilibrium positions.
  - This potential energy of interaction has a significant effect on the structure of a condensed phase.

Thermodynamic Properties of Liquids

- Liquids exist over a limited range of temperatures and pressures.
- Consider pressure exerted by a liquid at temperature T.
    - If this liquid is in equilibrium with its vapour, then the pressure of the vapour and of the liquid must be equal.
    - The boundary separating a liquid and a gas may be considered a deformable boundary that permits the transfer of energy and matter.
    - When a liquid and vapour are in equilibrium, the pressure is denoted by p_σ, which is a function of temperature.
    - If an inert gas that is insoluble in the liquid is present, the vapour phase will have two components and p_σ is a function of temperature and the applied pressure.

- At equilibrium, the chemical potential of the vapour and liquid are equal:

$$\mu_L = \mu^*(T) + RT \ln \frac{p_\sigma}{\mathcal{P}}$$

- The derivative of chemical potential with pressure is:

$$\left(\frac{\partial \mu_L}{\partial p}\right)_T = v_L$$

- Therefore:

$$RT \left(\frac{\partial \ln p_\sigma}{\partial p}\right)_T = v_L$$

  and the rate of change of vapour pressure with applied pressure may be determined.

- This equation is the Poynting equation.
- A typical molar volume is of the order of 100 cm^3.
  - At room temperature, $(\partial \ln p_\sigma / \partial p)_T$ is about 4 $\times 10^{-3}$ atm^{-1}.
- The temperature dependence of vapour pressure is determined by differences in entropy and molar volume of vapour and liquid.
- Consider the pressure temperature curve for coexistence of liquid and vapour.
  - Since the chemical potentials of liquid and vapour are equal on this curve,

$$d\mu^G = d\mu^L$$

$$-s^G dT + v^G dp_\sigma = -s^L dT + v^L dp_\sigma$$

- This can be rearranged to:

$$\left(\frac{\partial p}{\partial T}\right)_\sigma = \frac{s^G - s^L}{v^G - v^L}$$

which is the Clausius-Clapeyron equation.

- If the system is far from the critical point, $s^G > s^L$ and $v^G > v^L$ and

$$\left(\frac{\partial p}{\partial T}\right)_\sigma \approx \frac{s^G}{v^G}$$

- Consider the thermal pressure coefficient for a liquid:

$$\gamma_V \equiv \left(\frac{\partial p}{\partial T}\right)_V$$

- This is related to the dependence of the internal energy on volume.

$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

- The temperature dependence of γ_v is shown in Figure 23.2 (a).
  - For gas in equilibrium with liquid, $\gamma_\sigma = (\partial p/\partial T)_\sigma$ increases smoothly with temperature.
  - The dark solid lines are γ_v for liquid on the coexistence curve.
  - The lines on the right hand side are γ_v for various values of v and have slight temperature dependence.
    - The deviation from zero slope for temperature dependence indicates deviation of the fluid from ideality.

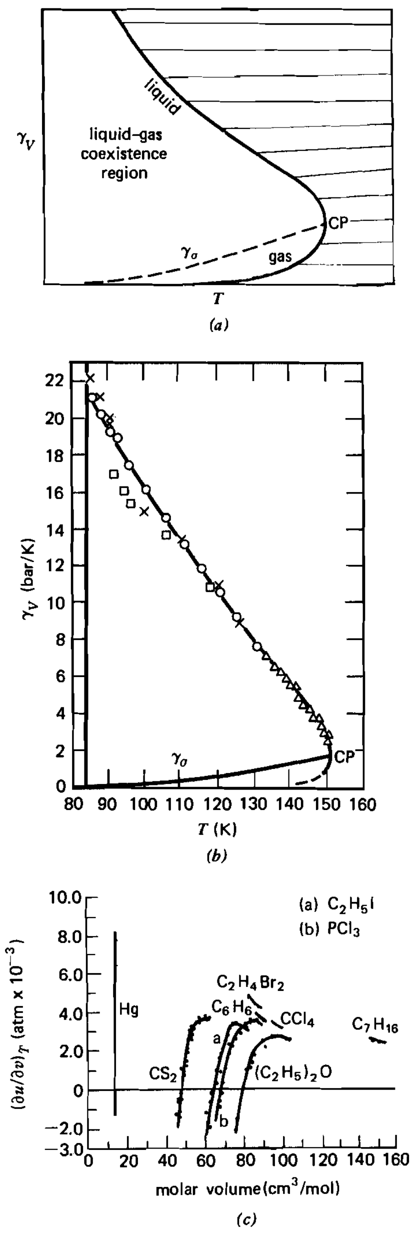

Figure 23.2 (*a*) The variation of the thermal pressure coefficient with temperature for the saturated gas and liquid, and for the homogeneous fluid at temperatures above saturation. (*b*) Thermal pressure coefficient of argon. From J. S. Rowlinson, *Liquids and Liquid Mixtures,* 2nd ed. (Butterworths, London, 1969). (*c*) $(\partial u/\partial v)_T$ as a function of molar volume. From J. H. Hildebrand and R. L. Scott, *Regular Solutions* (Prentice-Hall, Englewood Cliffs, N.J., 1962).

- The sign of γ_v is determined by the sign of α, the coefficient of thermal expansion.
- It may be shown:

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{(\partial v/\partial T)_p}{(\partial v/\partial p)_T} = \frac{\alpha}{\kappa_T}$$

  - κ is always positive.
  - α may be negative or positive.
  - Therefore α and γ_V have the same sign.
- Determination of $(\partial p/\partial T)_V$ from p, v, T properties of liquids lead to some generalizations.
  - κ_T decreases with increasing pressure, with rate of decrease decreasing as pressure increases.
  - κ_T increases with temperature, with the effect most pronounced at low pressure.

- α increases as temperature increases.
- From this conclusions about μ may be reached.
  - If α is positive and since T is positive, γ_V is positive.
    - If p is low, then u will decrease as v decreases.
    - There will exist a pressure where $[T(\partial p/\partial T)_V - p]$ becomes zero.
    - At pressures above this pressure, $(\partial u/\partial v)_T$ is negative and repulsive forces will dominate over attractive forces.
    - In this case, energy flows out of the liquid during compression.
- There are no simple equations of state for a liquid, but there are some empirical ones.
- The virial equation.

- The Tait equation is:

$$\frac{v_0 - v}{v_0 p} = \frac{A}{B + p}$$

- The Huddleston equation is:

$$\ln\left(\frac{pv^{2/3}}{v_0^{1/3} - v^{1/3}}\right) = A + B(v_0^{1/3} - v^{1/3})$$

- In the latter two, v_0 is the molar volume at zero pressure and A and B are positive empirical constants.
- If the virial equation is used, then several terms may be necessary, particularly in high density regions above the critical temperature.

- For the virial equation, the order of the term may be connected to the number of molecules interacting.
- There is no physical interpretation for either the Tait or Huddleston equation.
- For liquids, c_p has a much stronger temperature dependence than c_v.
- As in the case of gases, it is possible to calculate thermodynamic properties from the equation of state and the temperature dependent heat capacity.
- Also, as in the case of gases, the perfect gas will be used to define a reference state.
- A residual function f^E is defined:

$$f^E(T,v) = \int_{\infty}^{v} \left[\left(\frac{\partial f}{\partial v} \right)_T - \left(\frac{\partial f}{\partial v} \right)_T^{perfect\ gas} \right] dv$$

- This will be considered in two steps.
  - The initial state is in the low pressure limit with infinite volume.
  - The vapour is compressed isothermally to a finite volume,v_G, which is the volume of the vapour phase at pressure p_σ and temperature T.
  - The second step is isothermal condensation to a liquid with volume v^L.
- Thus, when applied to enthalpy:

$$h^E(T,v) = \int_\infty^v \left[\left(\frac{\partial h}{\partial v} \right)_T - \left(\frac{\partial h}{\partial v} \right)_T^{perfect\ gas} \right] dv$$

$$= \int_\infty^v \left[T \left(\frac{\partial p}{\partial T} \right)_v + v \left(\frac{\partial p}{\partial v} \right)_T \right] dv + \Delta h_{vap}$$

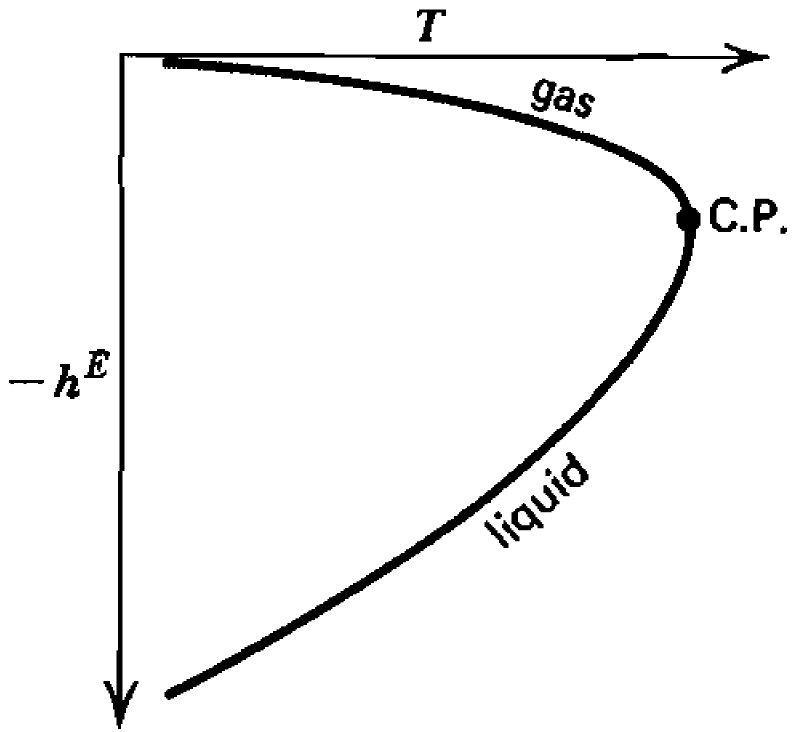

Figure 23.4 Sketch of the variation with temperature of the residual enthalpy of gas and liquid along the liquid–vapor coexistence curve. The difference between the two curves is the latent heat of evaporation. From J. S. Rowlinson, *Liquids and Liquid Mixtures,* 2nd ed. (Butterworths, London, 1969).

- h^E for liquid and vapour along the coexistence curve is shown in Figure 23.4.
- Note that the difference in h^E for the gas phase vanishes at the critical point.

Phase equilibria in One-Component systems

- When a phase transition occurs, there is a sudden change in physical and thermodynamic properties.
- The changes in enthalpy, entropy, and heat capacity are discontinuous.
- How and why do phase transitions occur?
  - Melting of solid.
  - Evaporation of liquid.
  - Sublimation of solid.