

Lecture Contents

3. The Second Law

Concentrating on the system

3.5 The Helmholtz and Gibbs energies

3.6 Standard reaction Gibbs energies

Combining the First and Second Laws

3.7 The fundamental equation

3.8 Properties of the internal energy

3.9 Properties of the Gibbs energy



Concentrating on the system

3.5 The Helmholtz and Gibbs energies

Consider a system in thermal equilibrium with its surroundings at T

If an energy is transferred as heat, **Clausius inequality** becomes $dS - \frac{dq}{T} \geq 0$

(a) Criteria for spontaneity

$$dS - \frac{dq}{T} \geq 0 \longrightarrow dS - \frac{dU}{T} \geq 0 \text{ or } TdS \geq dU \quad (\because dq_V = dU \text{ at constant volume, no additional work})$$

$$dS_{U,V} \geq 0 \text{ at } dU = 0, \quad dU_{S,V} \leq 0 \text{ at } dS = 0$$

$$\longrightarrow TdS \geq dH \quad (\because dq_p = dH \text{ at constant pressure, no additional work})$$

$$dS_{H,p} \geq 0 \text{ at } dH = 0, \quad dH_{S,p} \leq 0 \text{ at } dS = 0,$$

From $dU - TdS \leq 0$ and $dH - TdS \leq 0$,

Helmholtz energy (A) : $A = U - TS$

Gibbs energy (G) : $G = H - TS$

At constant T ,

$$(a) dA = dU - TdS \quad (b) dG = dH - TdS$$

The criteria of spontaneous change :

$$(a) dA_{T,V} \leq 0 \quad (b) dG_{T,p} \leq 0$$



3.5 The Helmholtz and Gibbs energies

(b) Some remarks on the Helmholtz energy

A spontaneous change of a system at const T and V if $dA_{T,V} \leq 0$

Criterion of equilibrium : $dA_{T,V} = 0$

Interpretation of $dA < 0$?

$$dA = dU - TdS$$

: Not lower internal energy but greater overall entropy

(c) Maximum work

$$dw_{\max} = dA \quad (\text{see justification 3.2})$$

A is sometimes called, 'maximum work function' or 'work function'
 $w_{\max} = \Delta A$ with $\Delta A = \Delta U - T\Delta S$

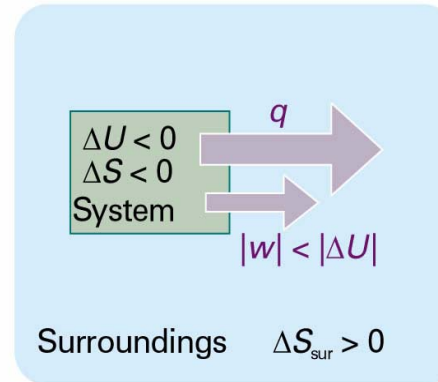


Fig. 3.15 In a system not isolated from its surroundings, the work done may be different from the change in internal energy. Moreover, the process is spontaneous if overall the entropy of the global, isolated system increases. In the process depicted here, the entropy of the system decreases, so that of the surroundings must increase in order for the process to be spontaneous, which means that energy must pass from the system to the surroundings as heat. Therefore, less work than ΔU can be obtained.

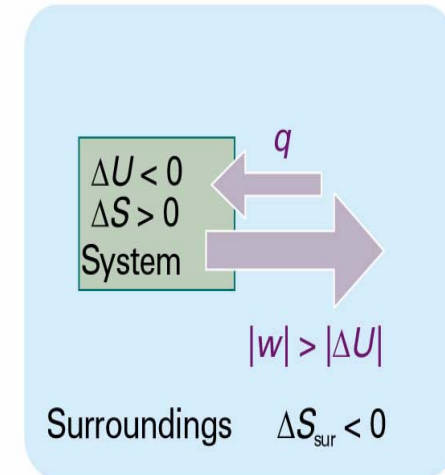


Fig. 3.16 In this process, the entropy of the system increases; hence we can afford to lose some entropy of the surroundings. That is, some of their energy may be lost as heat to the system. This energy can be returned to them as work. Hence the work done can exceed ΔU .



3.5 The Helmholtz and Gibbs energies

Justification 3.2 Maximum work

Clausius inequality : $dS - \frac{dq}{T} \geq 0$ or $TdS \geq dq$

Using the first law $dU = dq + dw$,

$$dU \leq TdS + dw$$

$$dw \geq dU - TdS$$

$$dw_{\max} = dU - TdS$$

At constant temperature, $dA = dU - TdS$,

$$dw_{\max} = dA$$



3.5 The Helmholtz and Gibbs energies

(d) Some remarks on the Gibbs energy

$dG_{T,p} \leq 0$: At constant T and p , chemical reactions are spontaneous in the direction of decreasing Gibbs energy.

$G \downarrow$: spontaneous tendency to convert the reactants into products

$G \uparrow$: reverse reaction is spontaneous

In $dG = dH - TdS$,

$dH > 0, dH < TdS \rightarrow dG < 0$: spontaneous endothermic reaction

(e) Maximum non-expansion work

At constant T and p , the maximum additional work ($w_{add,max}$) :

$$dw_{add,max} = dG \quad \text{or} \quad w_{add,max} = \Delta G$$

: useful expression for assessing the electrical work



3.5 The Helmholtz and Gibbs energies

Justification 3.3 Maximum non-expansion work

Because $H = U + pV$ and $dU = dq + dw$,

$$dH = dq + dw + d(pV)$$

The corresponding change in Gibbs energy ($G = H - TS$),

$$dG = dH - TdS - SdT = dq + dw + d(pV) - TdS - SdT$$

$$dG = dq + dw + d(pV) - TdS \quad \text{at } dT = 0 \text{ (isothermal),}$$

When the change is reversible, $dw = dw_{rev}$ and $dq = dq_{rev} = TdS$,

$$dG = TdS + dw_{rev} + d(pV) - TdS = dw_{rev} + d(pV)$$

At expansion work, $dw_{rev} = dw_{add,rev} - pdV$, and $d(pV) = pdV + Vdp$

$$dG = (-pdV + dw_{add,rev}) + pdV + Vdp = dw_{add,rev} + Vdp$$

At constant T and p ,

$$dw_{add, \max} = dG$$



3.6 Standard reaction Gibbs energies

Standard Gibbs energy of reaction, $(\Delta G^\circ)_r$:

The difference in standard molar Gibbs energies of the products and reactants in their standard states at the temperature specified for the reaction

$$(\Delta G^\circ)_r = (\Delta H^\circ)_r - T(\Delta S^\circ)_r$$

Standard Gibbs energy of formation, $(\Delta G^\circ)_f$:

The standard reaction Gibbs energy for the formation of a compound from its elements in their reference states

$$(\Delta G^\circ)_r = \sum_{\text{Products}} (\Delta G^\circ)_f - \sum_{\text{Reactants}} (\Delta G^\circ)_f$$

Synoptic Table 3.4* Standard Gibbs energies of formation (at 298 K)

	$\Delta_f G^\circ / (\text{kJ mol}^{-1})$
Diamond, C(s)	+2.9
Benzene, C ₆ H ₆ (l)	+124.3
Methane, CH ₄ (g)	-50.7
Carbon dioxide, CO ₂ (g)	-394.4
Water, H ₂ O(l)	-237.1
Ammonia, NH ₃ (g)	-16.5
Sodium chloride, NaCl(s)	-384.1

* More values are given in the *Data section*.



3.6 Standard reaction Gibbs energies

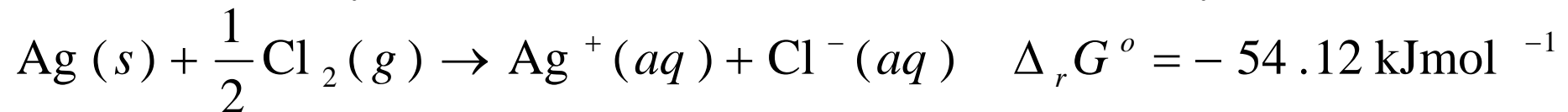
Illustration 3.7 (Calculating the standard Gibbs energy of reaction)

To calculate the standard Gibbs energy of the reaction $\text{CO(g)} + 1/2\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$ at 25°C , we write

$$\begin{aligned}\Delta_f G^\circ &= \Delta_f G^\circ(\text{CO}_2, \text{g}) - \left\{ \Delta_f G^\circ(\text{CO}, \text{g}) + \frac{1}{2} \Delta_f G^\circ(\text{O}_2, \text{g}) \right\} \\ &= -394.4 \text{ kJmol}^{-1} - \left\{ 137.2 + \frac{1}{2}(0) \right\} \text{ kJmol}^{-1} \\ &= -257.2 \text{ kJmol}^{-1}\end{aligned}$$

Illustration 3.8 (Calculating the standard Gibbs energy of formation of an ion)

With the value of $\Delta_f G^\circ(\text{Cl}^-, \text{aq})$ established, we can find the value of $\Delta_f G^\circ(\text{Ag}^+, \text{aq})$ from



which leads to $\Delta_f G^\circ(\text{Ag}^+, \text{aq}) = +77.11 \text{ kJmol}^{-1}$



3.6 Standard reaction Gibbs energies

$$\Delta_f G^\circ(\text{Cl}^-, \text{aq}) = 1272 \text{kJmol}^{-1} + \Delta_{\text{solv}} G^\circ(\text{H}^+) + \Delta_{\text{solv}} G^\circ(\text{Cl}^-)$$

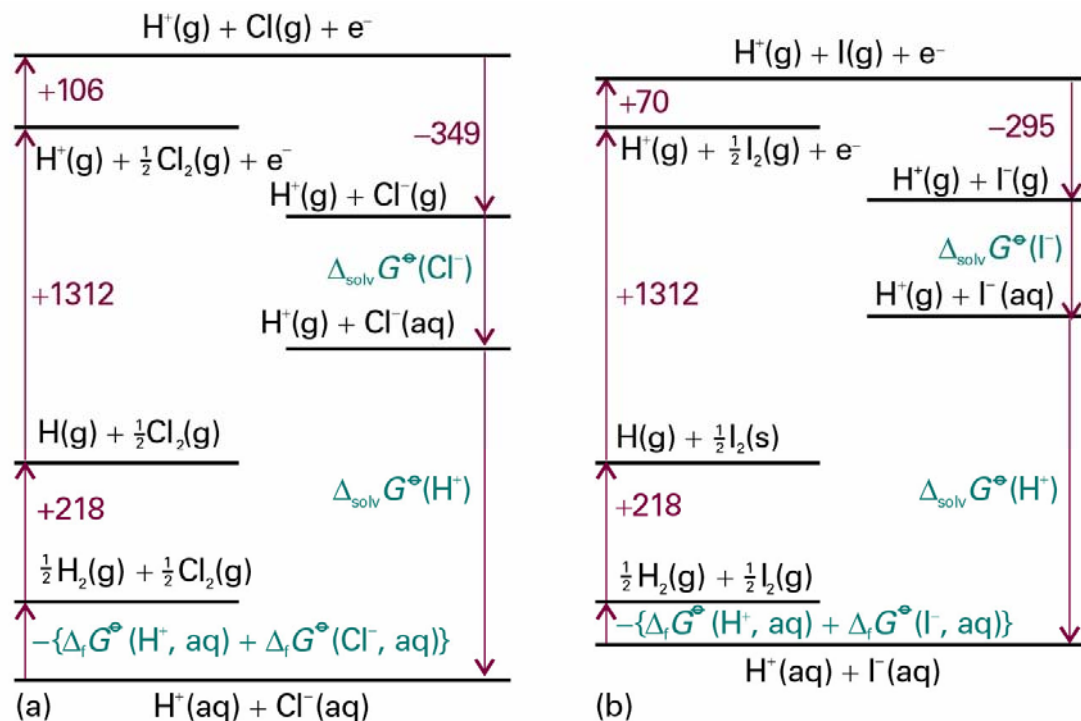


Fig. 3.17 The thermodynamic cycles for the discussion of the Gibbs energies of solvation (hydration) and formation of (a) chloride ions, (b) iodide ions in aqueous solution. The sum of the changes in Gibbs energies around the cycle sum to zero because G is a state function.

Comment 3.2

The standard Gibbs energies of formation of the gas-phase ions are unknown. We have therefore used ionization energies or electron affinities and have assumed that **any differences from the Gibbs energies** arising from conversion to enthalpy and the inclusion of entropies to obtain Gibbs energies in the formation of H^+ are cancelled.



Combining the First and Second Laws

3.7 The fundamental equation

1st law of thermodynamics : $dU = dq + dw$

For a reversible change in a closed system of constant composition, and in the absence of any additional (non-expansion) work,

$$dw_{rev} = -pdV \quad dq_{rev} = TdS$$

Therefore, for a reversible change in a closed system,

$$dU = TdS - pdV$$

This equation applies to any change – reversible or irreversible-of a system that does do no additional (non-expansion) work

This **fundamental equation** applies to both reversible and irreversible changes :

- For a reversible change : $TdS = dq$ and $-pdV = dw$
- For an irreversible change : $TdS > dq$ and $-pdV < dw$
 $\Rightarrow dw + dq = TdS - pdV$ provided the composition is constant.



3.8 Properties of the internal energy

As a function of S and V ; $U(S, V)$

$$dU = \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV \rightarrow \text{Since } dU = TdS - pdV, \quad \left(\frac{\partial U}{\partial S} \right)_V = T \quad \left(\frac{\partial U}{\partial V} \right)_S = -p$$

Thermodynamic definition of Temperature : The ratio of the changes in the internal energy and entropy of a constant volume, closed, constant-composition system

(a) The Maxwell relations

Suppose $df = gdx + hdy$,

$$\left(\frac{\partial g}{\partial y} \right)_x = \left(\frac{\partial h}{\partial x} \right)_y : \text{The mathematical criterion for } df \text{ being an exact differential}$$

Therefore, from the fundamental eqn. $dU = TdS - pdV$

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_V \quad : \text{Maxwell relation}$$

The expressions for dH , dA and dG (see Table 3.5)

Table 3.5 The Maxwell relations

From U :	$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_V$	$dU = TdS - pdV$
From H :	$\left(\frac{\partial T}{\partial p} \right)_S = \left(\frac{\partial V}{\partial S} \right)_p$	$dH = TdS + Vdp$
From A :	$\left(\frac{\partial p}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T$	$dA = -pdV - SdT$
From G :	$\left(\frac{\partial V}{\partial T} \right)_p = - \left(\frac{\partial S}{\partial p} \right)_T$	$dG = Vdp - SdT$



3.8 Properties of the internal energy

(b) The variation of internal energy with volume

$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T$: The internal pressure, π_T , representing how U changes as V of a system is changed isothermally, played a central role in the manipulation of the 1st law

$\pi_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$: Thermodynamic equation of state (see the Justification 3.4)

Justification 3.4 The Thermodynamic equation of state

$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$ → By dividing both sides by dV , $\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T + \left(\frac{\partial U}{\partial V}\right)_S$

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

By the Maxwell relation $\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$ → $\pi_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$



3.9 Properties of the Gibbs energy

(a) General considerations

$$dG = dH - TdS - SdT$$

Because $H = U + pV$, $dH = dU + pdV + Vdp$

By $dU = TdS - pdV$ in a closed system doing no additional work,

$$dG = (TdS - pdV) + pdV + Vdp - TdS - SdT$$

$$dG = Vdp - SdT$$

G : particularly suitable for chemical applications

As a function of p and T ; $G(p,T)$

$$dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT$$

Since $dG = Vdp - SdT$, $\left(\frac{\partial G}{\partial T}\right)_p = -S$ $\left(\frac{\partial G}{\partial p}\right)_T = V$

(See Fig. 3.18)

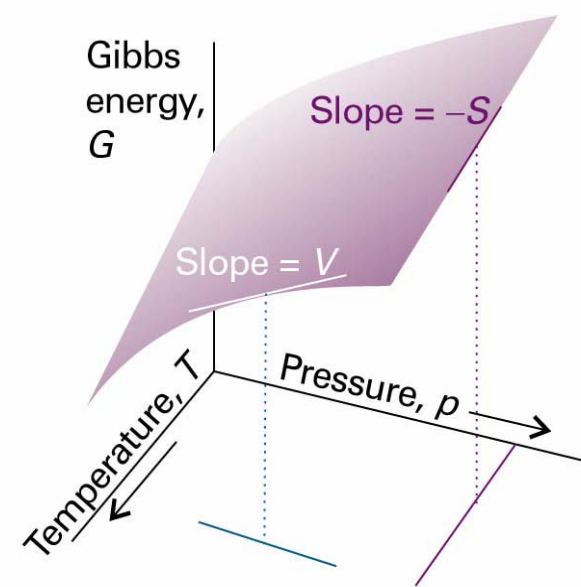


Fig. 3.18 The variation of the Gibbs energy of a system with (a) temperature at constant pressure and (b) pressure at constant temperature. The slope of the former is equal to the negative of the entropy of the system and that of the latter is equal to the volume.

3.9 Properties of the Gibbs energy

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

The Gibbs energy of the gaseous phase of a substance, which has a high molar entropy, is more sensitive to temperature than liquid and solid phases (See Fig. 3.19)

Because the molar volumes of gases are large, G is more sensitive to pressure for the gaseous phase of a substance than for its liquid and solid phases (See Fig. 3.20)

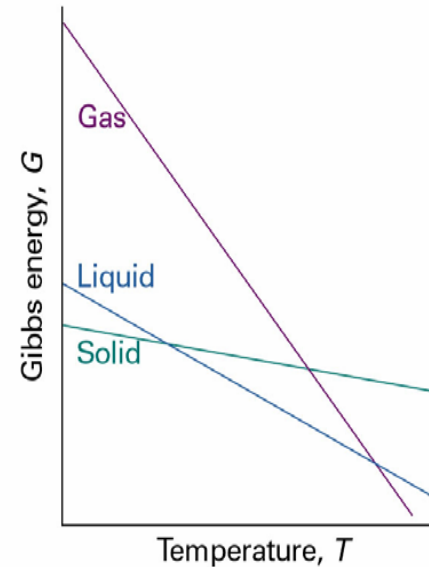


Fig. 3.19 The variation of the Gibbs energy with the temperature is determined by the entropy. Because the entropy of the gaseous phase of a substance is greater than that of the liquid phase, and the entropy of the solid phase is smallest, the Gibbs energy changes most steeply for the gas phase, followed by the liquid phase, and then the solid phase of the substance.

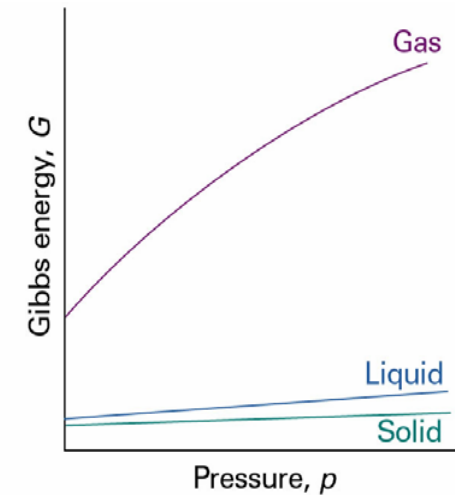


Fig. 3.20 The variation of the Gibbs energy with the pressure is determined by the volume of the sample. Because the volume of the gaseous phase of a substance is greater than that of the same amount of liquid phase, and the entropy of the solid phase is smallest (for most substances), the Gibbs energy changes most steeply for the gas phase, followed by the liquid phase, and then the solid phase of the substance. Because the volumes of the solid and liquid phases of a substance are similar, their molar Gibbs energies vary by similar amounts as the pressure is changed.



3.9 Properties of the Gibbs energy

(b) The variation of the Gibbs energy with temperature

Since $G = H - TS$ and then $S = (H - G)/T$,

$$\left(\frac{\partial G}{\partial T}\right)_p = -S = \frac{G - H}{T}$$

$$\rightarrow \left(\frac{\partial}{\partial T} \frac{G}{T}\right)_p = -\frac{H}{T^2} \quad \text{or} \quad \left(\frac{\partial}{\partial T} \frac{\Delta G}{T}\right)_p = -\frac{\Delta H}{T^2} \quad \text{Gibbs-Helmholtz equation}$$

: If we know H of the system, then we know how G/T varies with T

Justification 3.5

$$(1) \left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T} = -\frac{H}{T} \quad \left(\frac{\partial}{\partial T} \frac{G}{T}\right)_p = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_p + G \frac{d}{dT} \frac{1}{T} = \frac{1}{T} \left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2} = \frac{1}{T} \left\{ \left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T} \right\}$$

Since $\left(\frac{\partial G}{\partial T}\right)_p = \frac{G - H}{T} \therefore \left(\frac{\partial}{\partial T} \frac{G}{T}\right)_p = -\frac{H}{T^2}$

(2) Using the chain rule,

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = \left(\frac{\partial(G/T)}{\partial(1/T)}\right)_p \frac{d(1/T)}{dT} = \left(\frac{\partial(G/T)}{\partial(1/T)}\right)_p \times \left(-\frac{1}{T^2}\right)$$

Since $\left(\frac{\partial}{\partial T} \frac{G}{T}\right)_p = -\frac{H}{T^2} \therefore \left(\frac{\partial(G/T)}{\partial(1/T)}\right)_p = H$

<p>The chain rule :</p> <p>$f = f(g)$ and $g = g(t)$</p> $\frac{df}{dt} = \frac{df}{dg} \frac{dg}{dt}$
--



3.9 Properties of the Gibbs energy

(c) The variation of the Gibbs energy with pressure

At $dT = 0$ $p_i \rightarrow p_f$ $G(p_f) = G(p_i) + \int_{p_i}^{p_f} V dp$

For a liquid or solid, the volume changes only as the pressure changes. (See Fig. 3.21)

For molar quantities at constant V ,

$$G_m(p_f) = G_m(p_i) + V_m(p_f - p_i) = G_m(p_i) + V_m \Delta p$$

For a gas, G depends on p strongly.
 V varies obviously with p (not constant).
 (See Fig. 3.22)

For a perfect gas $V_m = RT/p$, RT : constant

$$G_m(p_f) = G_m(p_i) + RT \int_{p_i}^{p_f} \frac{dp}{p} = G_m(p_i) + RT \ln \frac{p_f}{p_i}$$

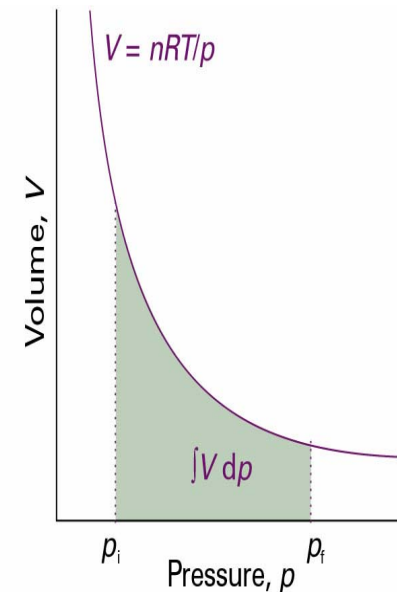
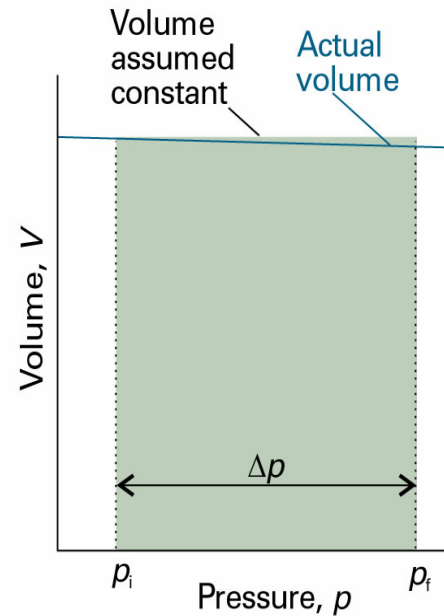


Fig. 3.21 The difference in Gibbs energy of a solid or liquid at two pressures is equal to the rectangular area shown. We have assumed that the variation of volume with pressure is negligible.

Fig. 3.22 The difference in Gibbs energy for a perfect gas at two pressures is equal to the area shown below the perfect-gas isotherm.



3.9 Properties of the Gibbs energy

If we set $p_i = p^\circ$ (the standard pressure of 1bar),
the molar Gibbs energy of a perfect gas at pressure p :

$$G_m(p) = G_m^\circ + RT \ln \frac{p}{p^\circ}$$

Predicted logarithmic dependence of G_m on p (See Fig. 3.23)

Illustration 3.10 (Gibbs energies at high pressures)

Suppose that for a certain phase transition of a solid $\Delta_{\text{trs}} V = +1.0 \text{ cm}^3 \text{ mol}^{-1}$ independent of pressure. Then, for an increase in pressure to 3.0Mbar ($3.0 \times 10^{11} \text{ Pa}$) from 1.0 bar ($1.0 \times 10^5 \text{ Pa}$), the Gibbs energy of the transition changes from $\Delta_{\text{trs}} G(1\text{bar})$ to

$$\begin{aligned} \Delta_{\text{trs}} G(3\text{Mbar}) &= \Delta_{\text{trs}} G(1\text{bar}) + (1.0 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}) \times (3.0 \times 10^{11} \text{ Pa} - 1.0 \times 10^5 \text{ Pa}) \\ &= \Delta_{\text{trs}} G(1\text{bar}) + 3.0 \times 10^2 \text{ kJ mol}^{-1} \end{aligned}$$

Where we have used $1 \text{ Pa m}^3 = 1 \text{ J}$

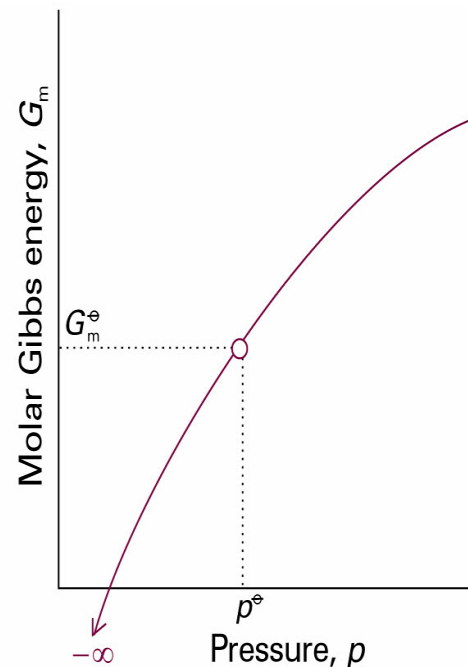


Fig. 3.23 The molar Gibbs energy potential of a perfect gas is proportional to $\ln p$, and the standard state is reached at p° . Note that, as $p \rightarrow 0$, the molar Gibbs energy becomes negatively infinite.

