**Introduction to Chemical Thermodynamics**

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First Year  
(13 Lectures)

**A. EQUILIBRIUM AND SPONTANEOUS CHANGE**

According to the first law of thermodynamics, the incremental change \( dU \) in the internal energy of a closed system during any physical or chemical process is given by

\[ dU = dq + dw, \]  
\[ (A1) \]

where \( dq \) is the heat added to the system and \( dw \) the work done on the system. According to the second law

\[ dS \geq \frac{dq}{T}, \]  
\[ (A2) \]

where \( dS \) is the change in the system entropy and \( T \) is the absolute temperature. The equality in Eq. (A2) applies to a reversible process and the inequality indicates the direction of spontaneous change.

It is useful to decompose the work done on the system into two contributions,

\[ dw = -p_{ex}dV + dw_e, \]  
\[ (A3) \]

where \( -p_{ex}dV \) is the expansion work associated with an incremental change in the system volume and \( dw_e \) is the remaining work (e.g., electrical work) done on the system by its surroundings. Since \( T \) is positive, Eq. (A2) implies that \( dq \leq TdS \), and combining this with Eqs. (A1) and (A3) gives

\[ dU \leq TdS - p_{ex}dV + dw_e. \]  
\[ (A4) \]

Hence for a system at constant entropy \( (dS = 0) \) and volume \( (dV = 0) \) that does not do any extra (non-\( pV \)) work on its surroundings \( (dw_e = 0) \) we have

\[ dU_{S,V} \leq 0, \]  
\[ (A5) \]

with \( dU_{S,V} = 0 \) at equilibrium.

Other more convenient conditions for equilibrium can be obtained by considering the three other energy state functions \( H, A, \) and \( G \). For example, since the enthalpy \( H \) is defined by

\[ H = U + pV, \]  
\[ (A6) \]

we have

\[ dH = dU + pdV + Vdp, \]  
\[ (A7) \]
and so for a system in mechanical equilibrium with its surroundings at pressure $p_{\text{ex}} = p$ it follows from Eq. (A4) that

$$dH \leq TdS + V dp + d\dot{w}_e.$$  \hfill (A8)

Hence for a constant-entropy and constant-pressure system that can only do $pV$ work on its surroundings

$$dH_{S,p} \leq 0,$$  \hfill (A9)

with $dH_{S,p} = 0$ at equilibrium.

In the same way, the definition of the Helmholtz free energy

$$A = U - TS,$$  \hfill (A10)

can be combined with Eq. (A4) to give

$$dA \leq -SdT - p_{\text{ex}} dV + d\dot{w}_e,$$  \hfill (A11)

so that at constant temperature and volume and in the absence of any extra work

$$dA_{T,V} \leq 0,$$  \hfill (A12)

with $dA_{T,V} = 0$ at equilibrium.

Finally, the definition of the Gibbs free energy

$$G = H - TS,$$  \hfill (A13)

leads (for a system in mechanical equilibrium with its surroundings – see Eq. (A8)) to

$$dG \leq -SdT + V dp + d\dot{w}_e,$$  \hfill (A14)

implying that at constant temperature and pressure and in the absence of any extra work

$$dG_{T,p} \leq 0,$$  \hfill (A15)

with $dG_{T,p} = 0$ at equilibrium.

Note that this last condition for equilibrium is especially convenient, because it is straightforward to fix both the temperature and the pressure of the system in a laboratory.

The physical interpretation of Eq. (A15) is as follows. In the absence of non-$pV$ work, the Gibbs free energy of the system decreases during any spontaneous process at constant temperature and pressure until equilibrium is achieved and the process can continue no further. The equation therefore allows us to calculate both the direction and the end point of a physical or chemical change within the system, but it does not tell us anything about the rate at which the change occurs.

When the system can do extra work on its surroundings (for example, when the system is an electrochemical cell harnessed to do electrical work in an external circuit), Eq. (A14) implies that

$$dG_{T,p} \leq d\dot{w}_e.$$  \hfill (A16)
It follows from this that if the Gibbs free energy of the system decreases by an incremental amount \( dG_{T,p} = -dW \) then \( d w_e \geq -dW \) and therefore \( -d w_e \leq dW \). Hence the decrease in the Gibbs free energy of the system can be interpreted as the maximum non-\( pV \) work that can be extracted from the system during a process at constant temperature and pressure, this maximum work being achieved by a reversible process. In the same way, the decrease in the Helmholtz free gives the maximum work that can be extracted during a process at constant \( T \) and \( V \).

Non-\( pV \) work is important in electrochemistry (see your Electrochemistry lectures later this year), but the remainder of these notes will be confined to the special case where \( pV \) work is the only possibility.

**B. FUNDAMENTAL EQUATIONS AND MAXWELL RELATIONS**

Now let us focus on a closed single-component system containing a fixed number of moles \( n \) of a single substance (e.g., a system containing one mole of water molecules). The reason for doing this is that the state of such a system is completely determined by specifying (e.g.) its volume and temperature, whereas additional composition variables are needed to specify the state of a multi-component system (see Section H).

According to Eq. (A4), the incremental change in the internal energy of the system during a reversible process that does not involve any non-expansion work is

\[
dU_{\text{rev}} = T dS - p dV,
\]

i.e., \( dU_{\text{rev}} = dq_{\text{rev}} + dw_{\text{rev}} \) where \( dq_{\text{rev}} = T dS \) and \( dw_{\text{rev}} = -pdV \). But since \( U(S,V) \) is a state function, changes in \( U \) are independent of the path taken (reversible or not) between one equilibrium state \((S, V)\) and another \((S + dS, V + dV)\), and so this last equation also applies more generally:

\[
dU = T dS - p dV.
\]

By the same argument, the inequalities in Eqs. (A8), (A11) and (A14) imply that

\[
dH = T dS + V dp,
\]

and

\[
dA = -SdT - p dV,
\]

and

\[
dG = -SdT + V dp.
\]

These four fundamental equations encapsulate what the first and second laws have to say about the variation of the four energy state functions with \( p \), \( V \), \( S \) and \( T \), and they are the basis of everything that follows. However, there is one important point that needs to be clarified before we go any further.

We have already seen [in Eq. (A15)] that if \( dw_e = 0 \) then \( dG_{T,p} < 0 \) for an irreversible change, whereas Eq. (B5) seems to imply that \( dG_{T,p} = 0 \) for all changes at constant \( T \) and \( p \). How can this be? The key point is that the equalities in this section assume that the system is in an equilibrium state both before and after the change, whereas the inequalities in Section A apply more generally. A mole of liquid water will...
spontaneously freeze at $-5\,^\circ\text{C}$ and one atmosphere pressure, for example, because this will lower its Gibbs free energy $[dG_{T,p} < 0]$. But since a mole of liquid water is not initially in equilibrium at this temperature and pressure, we have no reason to expect Eq. (B5) to apply to this situation and hence no reason to expect that $dG_{T,p} = 0$.

Let us now examine the implications of Eqs. (B2) to (B5). Since $U(S,V)$ is a state function, we know that

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \quad (B6)$$

is an exact differential, and (therefore – see your mathematics lecture notes) that

$$\left[\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right)_V\right]_S = \left[\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V}\right)_S\right]_V. \quad (B7)$$

Comparing Eq. (B6) with Eq. (B2) we find that

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_S = -p, \quad (B8)$$

and thus, in light of Eq. (B7), that

$$\left(\frac{\partial T}{\partial S}\right)_V = -\left(\frac{\partial p}{\partial S}\right)_V. \quad (B9)$$

Equation (B9) is the **Maxwell relation** associated with the fundamental equation for $dU$ in Eq. (B2). Each of the three other fundamental equations also has its own Maxwell relation, as summarised in the following table:

<table>
<thead>
<tr>
<th>Fundamental equation</th>
<th>Implication</th>
<th>Maxwell relation</th>
</tr>
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</table>

Note the various senses in which $S$ is conjugate to $T$ and $V$ is conjugate to $p$ in this table; since each of these conjugate pairs comprises one extensive ($S, V$) and one intensive ($T, p$) property, the energy functions $U, H, A$ and $G$ are all extensive (i.e., proportional to the amount of substance, $n$, in the system).

**C. EQUATIONS OF STATE**

Although it is “natural” in view of the above equations to regard $U$ as a function of $S$ and $V$, $H$ as a function of $S$ and $p$, $A$ as a function of $T$ and $V$, and $G$ as a function of $T$ and $p$, each of the four energy state functions can in fact be regarded as a function of any pair of variables selected from $p, V, S$ and $T$. 

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For example, since the entropy $S$ is a state function (a function of the state $V,T$ of the system), we know that

$$dS = \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV$$

(C1)

and hence from Eq. (B2) that

$$dU = TdS - pdV = T \left( \frac{\partial S}{\partial T} \right)_V dT + \left[ T \left( \frac{\partial S}{\partial V} \right)_T - p \right] dV.$$  

(C2)

Thus the internal energy $U$ can also be regarded as a function of $T$ and $V$:

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV,$$

(C3)

where

$$\left( \frac{\partial U}{\partial T} \right)_V = T \left( \frac{\partial S}{\partial T} \right)_V$$

(C4)

and

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

(C5)

This last equation can be simplified further by using the Maxwell relation in Eq. (B12) to give

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

(C6)

which rearranges to an equation of state of the form $p = p(V,T)$:

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

(C7)

In view of its derivation, this equation applies to all phases of all pure substances, with different phases and different substances giving different expressions for the partial derivatives $(\partial p/\partial T)_V$ and $(\partial U/\partial V)_T$ (i.e., different equations of state). The simplest example is the perfect gas equation $p = nRT/V$, which gives $(\partial p/\partial T)_V = nR/V$ and hence the important result that

$$\left( \frac{\partial U}{\partial V} \right)_T = 0$$

for a perfect gas.  

(C8)

D. A DIRTY TRICK

Equation (C4) can be obtained with less effort by dividing $dU = TdS - pdV$ throughout by $dT$ at constant $V$, and then noting that $(\partial V/\partial T)_V = 0$:

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

(D1)

In the same way, Eq. (C5) can be obtained by dividing $dU = TdS - pdV$ through by $dV$ at constant $T$, and then noting that $(\partial V/\partial V)_T = 1$:

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

(D2)
It is not strictly legitimate to divide by differentials like this, but the trick can nevertheless be justified on the basis of the **chain rule** for partial differentiation (see your mathematics lecture notes):

\[
\left( \frac{\partial U}{\partial X} \right)_Y = \left( \frac{\partial U}{\partial S} \right)_V \left( \frac{\partial S}{\partial X} \right)_Y + \left( \frac{\partial U}{\partial V} \right)_S \left( \frac{\partial V}{\partial X} \right)_Y \equiv T \left( \frac{\partial S}{\partial X} \right)_Y - p \left( \frac{\partial V}{\partial X} \right)_Y.
\]

(D3)

with \((X,Y) = (T,V)\) in Eq. (D1) and \((X,Y) = (V,T)\) in Eq. (D2). We shall use this trick repeatedly in the following section.

### E. HEAT CAPACITIES

Let us now consider the relationship between the constant-volume and constant-pressure heat capacities

\[
C_V = \left( \frac{\partial U}{\partial T} \right)_V \quad \text{and} \quad C_p = \left( \frac{\partial H}{\partial T} \right)_p.
\]

(E1)

From Eq. (D1), we already know that

\[
C_V = \left( \frac{\partial U}{\partial T} \right)_V = T \left( \frac{\partial S}{\partial T} \right)_V,
\]

(E2)

and dividing \(dH = TdS + Vdp\) through by \(dT\) at constant \(p\) we find that

\[
C_p = \left( \frac{\partial H}{\partial T} \right)_p = T \left( \frac{\partial S}{\partial T} \right)_p.
\]

(E3)

Hence

\[
C_p - C_V = T \left[ \left( \frac{\partial S}{\partial T} \right)_p - \left( \frac{\partial S}{\partial T} \right)_V \right].
\]

(E4)

In order to simplify this result, we can divide the expression for \(dS\) in Eq. (C1), \(dS = (\partial S/\partial T)_V dT + (\partial S/\partial V)_T dV\), through by \(dT\) at constant \(p\) to obtain

\[
\left( \frac{\partial S}{\partial T} \right)_p = \left( \frac{\partial S}{\partial T} \right)_V + \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p,
\]

(E5)

and hence

\[
C_p - C_V = T \left[ \left( \frac{\partial S}{\partial T} \right)_T \left( \frac{\partial V}{\partial T} \right)_p \right].
\]

(E6)

The final simplification is to use the Maxwell relation in Eq. (B12) to replace \((\partial S/\partial V)_T\) with \((\partial p/\partial T)_V\):

\[
C_p - C_V = T \left( \frac{\partial p}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_p.
\]

(E7)

Using this final form, it is easy to calculate the difference between the constant-pressure and constant-volume heat capacities of any system for which we know the equation of state. For example, the perfect gas equation \(pV = nRT\) gives

\[
\left( \frac{\partial p}{\partial T} \right)_V = \frac{nR}{V} \quad \text{and} \quad \left( \frac{\partial V}{\partial T} \right)_p = \frac{nR}{p}.
\]

(E8)
and hence (since $nRT/pV = 1$)

$$C_p - C_V = nR. \quad (E9)$$

Note also that the definition of $C_p$ in Eq. (E1) can be integrated at constant pressure to give

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p(T) \, dT, \quad (E10)$$

and that Eq. (E3) integrates to

$$S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{C_p(T)}{T} \, dT. \quad (E11)$$

Since these equations apply to any closed single-component system, and a chemical reaction under standard conditions boils down to a collection of independent single-component systems ($\phi = \text{pure substance at a pressure of 1 bar}$), it immediately follows (by addition of the products and subtraction of the reactants) that

$$\Delta_r H^\phi (T_2) = \Delta_r H^\phi (T_1) + \int_{T_1}^{T_2} \Delta C_p(T) \, dT, \quad (E12)$$

and

$$\Delta_r S^\phi (T_2) = \Delta_r S^\phi (T_1) + \int_{T_1}^{T_2} \frac{\Delta C_p(T)}{T} \, dT, \quad (E13)$$

where $\Delta_r H^\phi (T)$ is the standard reaction enthalpy, $\Delta_r S^\phi (T)$ is the standard reaction entropy, and

$$\Delta C_p(T) = \sum J \nu_J C_{p,m}(J; T), \quad (E14)$$

with the $\nu_J$’s being the stoichiometric coefficients of the reaction (e.g., $\nu_{\text{NH}_3} = +2$, $\nu_{\text{N}_2} = -1$ and $\nu_{\text{H}_2} = -3$ for the reaction $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$). Equation (E12) is Kirchhoff’s Law.

F. PROPERTIES OF THE GIBBS FREE ENERGY

The temperature and pressure-dependence of the Gibbs free energy $G$ follow directly from the fundamental equation $dG = -SdT + Vdp$ in Eq. (B5), which implies that

$$\left( \frac{\partial G}{\partial T} \right)_p = -S \quad \text{and} \quad \left( \frac{\partial G}{\partial p} \right)_T = V. \quad (F1)$$

Since $G = H - TS$, the first of these equations can be re-written as

$$\left( \frac{\partial G}{\partial T} \right)_p = \frac{G - H}{T}, \quad (F2)$$

or equivalently

$$\left( \frac{\partial G}{\partial T} \right)_p - \frac{G}{T} = -\frac{H}{T}. \quad (F3)$$

The idea now is to find a more convenient expression for the left-hand side, which can be accomplished by noting that

$$\left( \frac{\partial G/T}{\partial T} \right)_p = \frac{1}{T} \left( \frac{\partial G}{\partial T} \right)_p - \frac{G}{T^2} = \frac{1}{T} \left[ \left( \frac{\partial G}{\partial T} \right)_p - \frac{G}{T} \right]. \quad (F4)$$
Combining this with Eq. (F3) we obtain the **Gibbs-Helmholtz equation**, which relates the temperature-dependence of the Gibbs free energy to the system enthalpy (rather than the system entropy as in Eq. (F1)):

\[
\left( \frac{\partial (G/T)}{\partial T} \right)_p = \frac{H}{T^2}.
\] (F5)

Once again, this equation applies to any closed single-component system, and therefore (by addition of the products and subtraction of the reactants) to a chemical reaction under standard conditions:

\[
\left( \frac{\partial (\Delta_r G^\circ /T)}{\partial T} \right)_p = -\frac{\Delta_r H^\circ}{T^2}.
\] (F6)

Turning now to the pressure-dependence of the Gibbs energy, the second equation in (F1) can be integrated at constant temperature to give

\[
G(p_2, T) = G(p_1, T) + \int_{p_1}^{p_2} V(p, T) \, dp,
\] (F7)

which in the special case of one mole of a perfect gas becomes

\[
G_m(p_2, T) = G_m(p_1, T) + \int_{p_1}^{p_2} \frac{RT}{p} \, dp = G_m(p_1, T) + RT \ln \left( \frac{p_2}{p_1} \right).
\] (F8)

In particular, if we set \( p_2 = p \) and \( p_1 = p^\circ \) in this equation we get

\[
G_m(p, T) = G_m^\circ(T) + RT \ln \left( \frac{p}{p^\circ} \right),
\] (F9)

the significance of which will become apparent in Section H.

G. PHASE EQUILIBRIA

Suppose that two phases \( \alpha \) and \( \beta \) of a pure substance are in equilibrium at a specified temperature and pressure. Since the condition for equilibrium at constant \( p \) and \( T \) is \( dG_{p,T} = 0 \) [see Eq. (A15)], this implies that the change in the Gibbs free energy of the system on moving an infinitesimal amount of material \( dn \) from one phase to the other must be zero,

\[
dG_{p,T} = [G_{m,\beta} - G_{m,\alpha}] \, dn = 0,
\] (G1)

and hence that the molar Gibbs free energies of the two phases must be the same:

\[
G_{m,\alpha} = G_{m,\beta}.
\] (G2)

Since this equation imposes one constraint on the two variables (\( p \) and \( T \)) that are needed to specify the state of the system, it follows that equilibrium between two phases in a one-component system can only exist along certain lines (known as phase boundaries) in the two-dimensional \( p, T \) plane. If three phases \( \alpha, \beta \) and \( \gamma \) are simultaneously in equilibrium we have one additional constraint,

\[
G_{m,\alpha} = G_{m,\beta} = G_{m,\gamma},
\] (G3)
and so by the same argument this situation can only be realized at a single point in the $p, T$ plane (known as the triple point). Hence we have the following **phase rule** for a single-component system,

$$F = 3 - P,$$  \hspace{1cm} (G4)

where $F$ is the number of degrees of freedom – the number of directions in the $p, T$ plane we are free to move in without violating the equilibrium condition – and $P$ is the number of phases in equilibrium.

It is also possible to use thermodynamics to determine the slope $dp/dT$ of a phase boundary. Suppose that two phases $\alpha$ and $\beta$ are in equilibrium at a given $p$ and $T$, and that we change the pressure by a small amount $dp$ and the temperature by an amount $dT$. In view of Eq. (B5), the molar Gibbs energy of the $\alpha$ phase will change by

$$dG_{m,\alpha} = V_{m,\alpha} dp - S_{m,\alpha} dT,$$ \hspace{1cm} (G5)

and that of the $\beta$ phase by

$$dG_{m,\beta} = V_{m,\beta} dp - S_{m,\beta} dT.$$ \hspace{1cm} (G6)

Since the two phases are initially in equilibrium, we know that $G_{m,\alpha} = G_{m,\beta}$, and if they are to remain in equilibrium after the change we must have that $dG_{m,\alpha} = dG_{m,\beta}$. Hence by subtraction of Eq. (G5) from Eq. (G6) we find that

$$0 = \Delta V dp - \Delta S dT,$$ \hspace{1cm} (G7)

where $\Delta V = V_{m,\beta} - V_{m,\alpha}$ and $\Delta S = S_{m,\beta} - S_{m,\alpha}$. The slope of the phase boundary is therefore given by the **Clapeyron equation**

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V}.$$ \hspace{1cm} (G8)

This result can also be taken slightly further by noting that the definition of $G$ in Eq. (A13) implies

$$\Delta G = \Delta H - T \Delta S,$$ \hspace{1cm} (G9)

where $\Delta G = G_{m,\beta} - G_{m,\alpha}$ and $\Delta H = H_{m,\beta} - H_{m,\alpha}$. Since $\Delta G = 0$ at equilibrium [Eq. (G2)], we find that the entropy and enthalpy changes during a phase transition are related by

$$\Delta S = \frac{\Delta H}{T},$$ \hspace{1cm} (G10)

and hence that the Clapeyron equation can be written equivalently as

$$\frac{dp}{dT} = \frac{\Delta H}{T \Delta V}.$$ \hspace{1cm} (G11)

Both forms of the equation [(G8) and (G11)] are exact, and they apply to all phase equilibria in single-component systems ($s \leftrightarrow l$, $s \leftrightarrow g$, $l \leftrightarrow g$, diamond $\leftrightarrow$ graphite, etc.).

However, in the special case of sublimation ($s \leftrightarrow g$) and vaporization ($l \leftrightarrow g$) equilibria, we can make even more progress with the help of the following two simplifying approximations:

$$\Delta V = V_{m,g} - V_{m,\text{condensed}} \simeq V_{m,g},$$ \hspace{1cm} (G12)
and
\[ V_{m,g} \simeq \frac{RT}{p}. \]  
(G13)

Substituting these approximations into Eq. (G11) we obtain the **Clausius-Clapeyron equation**

\[ \frac{1}{p} \frac{dp}{dT} \equiv \frac{d\ln p}{dT} = \frac{\Delta H}{RT^2}, \]  
(G14)

which has a form that we can integrate along the phase boundary:

\[ \int_{p_1}^{p_2} \frac{1}{p} \, dp = \ln \left( \frac{p_2}{p_1} \right) = \int_{T_1}^{T_2} \frac{\Delta H}{RT^2} \, dT. \]  
(G15)

Assuming that \( \Delta H \) is independent of \( T \) over the temperature range \( T_1 \leq T \leq T_2 \) (another approximation), the right-hand side of this equation can be evaluated to give

\[ \ln \left( \frac{p_2}{p_1} \right) \simeq \frac{\Delta H}{R} \int_{T_1}^{T_2} \frac{1}{T^2} \, dT = \frac{\Delta H}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]. \]  
(G16)

Hence a plot of \( \ln p_2 \) vs \( 1/T_2 \) is expected to give a straight line with a slope of \(-\Delta H/R\); this provides a way to determine (e.g.) the latent heat of vaporization of a liquid, \( \Delta_{\text{vap}} H \), from measurements of its vapour pressure \( (p_2) \) as a function of temperature \( (T_2) \).

### H. CHEMICAL EQUILIBRIA

So far, we have focused exclusively on closed single-component systems, the Gibbs free energies \( G(p,T) \) of which depend solely on \( p \) and \( T \). However, systems in which chemical reactions can occur inevitably involve more than one component (chemical species), and in order to describe the state of such a system we must augment \( p \) and \( T \) with additional composition variables.

Now the Gibbs free energy of an open single-component system is a function \( G(n,p,T) \) of the state \( (n,p,T) \) of the system, that of a two-component system is a function \( G(n_1,n_2,p,T) \), and so on. In general, for a \( C \)-component system,

\[ G \equiv G(n,p,T), \]  
(H1)

where \( n \equiv \{ n_1, \ldots, n_C \} \) is a shorthand notation for the \( C \) composition variables. The fundamental equation \( dG = V \, dp - S \, dT \) for changes in \( G \), Eq. (B5), can also be generalized to the multi-component case, as follows:

\[ dG = V \, dp - S \, dT + \sum_J \mu_J \, dn_J, \]  
(H2)

where

\[ V = \left( \frac{\partial G}{\partial p} \right)_{T,n}, \]  
(H3)

and

\[ S = - \left( \frac{\partial G}{\partial T} \right)_{p,n}, \]  
(H4)

and

\[ \mu_J = \left( \frac{\partial G}{\partial n_J} \right)_{p,T,n'_J}, \]  
(H5)
with \( n'_j \) including all of the composition variables except for \( n_J \). Equation (H3) is the multi-component generalization of \( V = (\partial G/\partial p)_T \), Eq. (H4) generalizes \( S = -(\partial G/\partial T)_p \), and Eq. (H5) defines the chemical potential (partial molar Gibbs free energy) of component \( J \) in the multi-component system.

When a chemical reaction occurs within the system, the changes \( d n_J \) in the number of moles of each component in Eq. (H2) are related by stoichiometry. For example, consider a closed system containing the three components \( N_2(g), H_2(g) \) and \( NH_3(g) \), which are related by the reaction \( N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \). It is clear from the stoichiometry of this reaction that if \( d n_{NH_3} = +2d\xi \) then \( dn_{N_2} = -d\xi \) and \( dn_{H_2} = -3d\xi \), and hence in general that

\[
dn_J = \nu_J d\xi, \quad (H7)
\]

where \( \nu_J \) is the stoichiometric coefficient of component \( J \) and the variable \( \xi \) measures the extent of reaction (with the reactants at \( \xi = 0 \) and the products at \( \xi = 1 \)). This simple observation allows us to obtain conditions for both the equilibrium position and the direction of spontaneous change in the reaction.

From Eq. (H2), if the system is at constant temperature \((dT = 0)\) and pressure \((dp = 0)\) we have that

\[
dG_{T,p} = \sum_J \mu_J dn_J, \quad (H8)
\]

and substituting Eq. (H7) for \( dn_J \) we obtain

\[
dG_{T,p} = \sum_J \nu_J \mu_J d\xi. \quad (H9)
\]

If we now define the molar Gibbs energy of reaction as the derivative of the Gibbs energy of the system with respect to the extent of reaction at constant \( T \) and \( p \),

\[
\Delta_r G \equiv \left(\frac{\partial G}{\partial \xi}\right)_{T,p}, \quad (H10)
\]

then it follows from the general discussion of the condition \( dG_{T,p} \leq 0 \) on p. 2 that the reaction will proceed spontaneously (in the direction of increasing \( \xi \)) if \( \Delta_r G < 0 \) and that the condition for chemical equilibrium is \( \Delta_r G = 0 \). Furthermore, it is clear from Eq. (H9) that \( \Delta_r G \) is given by

\[
\Delta_r G = \sum_J \nu_J \mu_J, \quad (H11)
\]

which reduces to the expected result under standard conditions:

\[
\Delta_r G^\circ = \sum_J \nu_J \mu_J^\circ \equiv \sum_J \nu_J G^\circ_m(J). \quad (H12)
\]

Let us now consider the implications of the equilibrium condition, \( \Delta_r G = 0 \), for the special case of a reaction involving perfect gases, the chemical potentials (partial molar Gibbs free energies) of which satisfy [see Eq. (F9)]

\[
\mu_J = \mu_J^\circ + RT \ln \left( \frac{p_J}{p_J^\circ} \right). \quad (H13)
\]
Combining this with Eq. (H11) we obtain

\[ \Delta_r G = \sum_j \nu_j \mu_j \]

\[ = \sum_j \nu_j \mu_j^\circ + \sum_j \nu_j RT \ln \left( \frac{p_j}{p_j^\circ} \right) \]

\[ = \sum_j \nu_j \mu_j^\circ + RT \sum_j \ln \left( \frac{p_j}{p_j^\circ} \right)^{\nu_j} \]

\[ = \sum_j \nu_j \mu_j^\circ + RT \ln \left[ \prod_j \left( \frac{p_j}{p_j^\circ} \right)^{\nu_j} \right] , \]

\[ = \Delta_r G^\circ + RT \ln Q, \]

where

\[ Q = \prod_j \left( \frac{p_j}{p_j^\circ} \right)^{\nu_j} \]

is the reaction quotient [so called because it usually is a quotient rather than a product; for the reaction \( \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \), for example, we have

\[ Q = \left( \frac{p_{\text{NH}_3}}{p_{\text{N}_2}^\circ} \right)^2 \left( \frac{p_{\text{N}_2}}{p_{\text{N}_2}^\circ} \right)^{-1} \left( \frac{p_{\text{H}_2}}{p_{\text{N}_2}^\circ} \right)^{-3} = \left( \frac{p_{\text{NH}_3}/p_{\text{N}_2}^\circ}{p_{\text{N}_2}/p_{\text{N}_2}^\circ} \right)^2 \left( \frac{p_{\text{H}_2}/p_{\text{N}_2}^\circ}{p_{\text{H}_2}/p_{\text{N}_2}^\circ} \right)^3 . \]

Imposing the condition for chemical equilibrium, \( \Delta_r G = 0 \), in Eq. (H14) gives

\[ \Delta_r G^\circ = -RT \ln K, \]

where \( K = Q_{\text{eqm}} \) is the equilibrium constant

\[ K = \left[ \prod_j \left( \frac{p_j}{p_j^\circ} \right)^{\nu_j} \right]_{\text{eqm}} . \]

Note that this equilibrium constant is dimensionless, that its temperature-dependence can be obtained by combining Eqs. (F6) and (H16) to give the van’t Hoff equation

\[ \left( \frac{\partial \ln K}{\partial T} \right)_p = \frac{\Delta_r H^\circ}{RT^2} , \]

and that it is independent of the pressure of the system (from Eq. (H16), \( K = e^{-\Delta_r G^\circ /RT} \) depends on \( p^\circ \) rather than \( p \)). The yield of the reaction at equilibrium does however depend on pressure, as expected from Le Chatelier’s principle - see your lecture notes for a worked example.