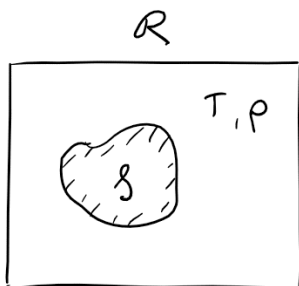# Lecture 11 – Gibbs free energy

PREVIOUSLY: In Lect. 9 we introduced the thermodynamics potentials, including the Gibbs free energy, $G \equiv \underbrace{U + pV}_{H} - TS$, which is useful for systems maintained at constant T and p.

TODAY: <u>Gibbs free energy</u>
What are the equilibrium properties of systems at constant T and p?

Consider a system $\mathcal{S}$ that is held at constant T and p by a reservoir $\mathcal{R}$ (e.g. the atmosphere)

Recall the identity:

$$dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV = \frac{1}{T}dU + \frac{p}{T}dV$$

The total system $\mathcal{R} + \mathcal{S}$ is closed so its entropy is an extremum at equilibrium:

$$dS_{\mathcal{R}+\mathcal{S}} = 0 = dS_{\mathcal{R}} + dS_{\mathcal{S}}$$

$$= \frac{dU_{\mathcal{R}}}{T_{\mathcal{R}}} + \frac{p_{\mathcal{R}}}{T_{\mathcal{R}}}dV_{\mathcal{R}} + dS_{\mathcal{S}} \quad \text{but } dU_{\mathcal{R}} = -dU_{\mathcal{S}} \text{ since } U = U_{\mathcal{R}} + U_{\mathcal{S}} \text{ is fixed}$$

$$\text{and } dV_{\mathcal{R}} = -dV_{\mathcal{S}} \text{ since } V = V_{\mathcal{R}} + V_{\mathcal{S}} \text{ is fixed}$$

$$= -\frac{dU_{\mathcal{S}}}{T} - \frac{p}{T}dV_{\mathcal{S}} + dS_{\mathcal{S}} \quad \text{since } T = T_{\mathcal{S}} = T_{\mathcal{R}} \text{ and } p = p_{\mathcal{S}} = p_{\mathcal{R}}$$

$$= -\frac{1}{T}d(U_{\mathcal{S}} + pV_{\mathcal{S}} - TS_{\mathcal{S}})$$

$$\uparrow$$

This quantity is a property of $\mathcal{S}$ alone.

So, if $S_{\mathcal{R}+\mathcal{S}}$ is an extremum, so must $U_{\mathcal{S}} + pV_{\mathcal{S}} - TS_{\mathcal{S}}$ be an extremum by this equality.
Define <u>Gibbs free energy</u> $G \equiv U + pV - TS$ such that $dS_{\mathcal{R}+\mathcal{S}} = 0 = -dG_{\mathcal{S}}$ at equilibrium.

$S_{\mathcal{R}+\mathcal{S}}$ is a <u>maximum</u>, but $G_{\mathcal{S}}$ is a <u>minimum</u>, due to $-$ sign (like the Helmholtz free energy)

So, in a constant p, T ensemble, G of system $\mathcal{S}$ tends to <u>decrease</u> until it reaches a minimum at equilibrium.
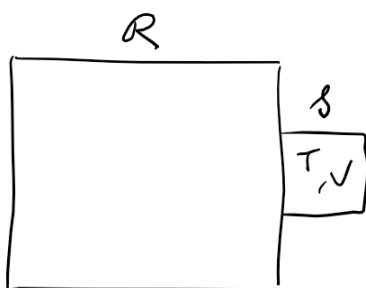
To recap the different ensembles:
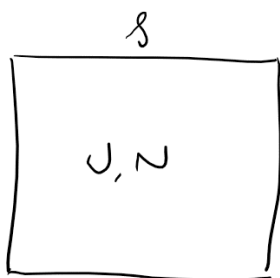
<u>Microcanonical ensemble</u>

System $\mathfrak{S}$ is closed: fixed $U_{\mathfrak{S}}$, $V_{\mathfrak{S}}$

Entropy $S_{\mathfrak{S}}$ increases: $\Delta S_{\mathfrak{S}} \geq 0$ (= 0 at equilibrium)
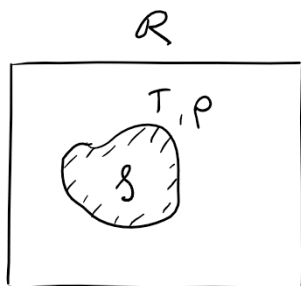
<u>Canonical ensemble</u>

System $\mathfrak{S}$ is in thermal contact with reservoir $\mathcal{R}$:
fixed $T = T_{\mathfrak{S}} = T_{\mathcal{R}}$, $V_{\mathfrak{S}}$

Helmholtz free energy $F_{\mathfrak{S}}$ decreases: $\Delta F_{\mathfrak{S}} \leq 0$ (= 0 at equilibrium)

System $\mathfrak{S}$ is in thermal contact with reservoir $\mathcal{R}$ at constant pressure: fixed $T = T_{\mathfrak{S}} = T_{\mathcal{R}}$, $p = p_{\mathfrak{S}} = p_{\mathcal{R}}$

Gibbs free energy $G_{\mathfrak{S}}$ decreases: $\Delta G_{\mathfrak{S}} \leq 0$ (= 0 at equilibrium)

Also showed that:

$U = U(S,V)$ $\qquad\qquad\qquad\qquad dU = TdS - pdV + \mu dN$

$F = F(T,V) \equiv U - TS$ $\qquad\qquad dF = -pdV - SdT + \mu dN$

$G = G(p,T) \equiv U + pV - TS = H - TS$ $\qquad dG = -SdT + Vdp + \underbrace{\mu dN}$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ We add this term when
$\qquad\qquad\qquad\qquad\qquad\qquad$ particles can be exchanged

We also related these quantities to work:

$W \geq \Delta F$

$W' \geq \Delta G$ ($W' \equiv W + p\Delta V$ is the effective work, i.e. work <u>other</u> than that done automatically by
$\qquad$ the atmosphere $-p\Delta V$)

(= when process is reversible throughout, i.e. at equilibrium throughout)

KEY CONCEPT: Relationship between Gibbs free energy and chemical potential

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Question 1: Derive the Gibbs free energy _G_ for a monatomic ideal gas.

$G = U + pV - TS$

For an ideal gas, $U = \frac{3}{2}Nk_B T$, $pV = Nk_B T$, and $S = Nk_B \left(\ln \frac{n_Q}{n} + \frac{5}{2} \right)$ so

$$G_{ideal} = \frac{3}{2}Nk_B T + Nk_B T - Nk_B T \left(\ln \frac{n_Q}{n} + \frac{5}{2} \right) = Nk_B T \ln \frac{n}{n_Q}$$

Recall the chemical potential for the ideal gas: $\mu_{ideal} = k_B T \ln \frac{n}{n_Q}$

so $G_{ideal} = N \mu_{ideal}$.

This relationship turns out to be true <u>generally</u>.

<u>Proof</u>: Recall extensive/intensive quantities – extensive quantities scale linearly with system size, intensive quantities are independent.

Question 2: Classify the following thermodynamic quantities as extensive or intensive: _U, S, F, T, p, V, n = N/V,_ and _μ_

Extensive quantities will double if $N \rightarrow 2N$, $V \rightarrow 2V$, $U \rightarrow 2U$, intensive quantities will remain the same

Extensive: _U, S, F, V_   Intensive: _T, p, n, μ_

Note that if follows that $G = U + pV - TS$ is extensive

If we double the system size: $G(T,p,N) \rightarrow 2G(T,p,N \rightarrow 2N)$. Since _T, p_ are intensive it must be that $G \propto N$, i.e.

$$G = N\varphi(T,p)$$

The next step is proving that $\varphi(T,p) = \mu(T,p)$:

$$dG = -SdT + Vdp + \mu dN \quad \text{so} \quad \left(\frac{\partial G}{\partial N}\right)_{T,p} = \mu$$

and

$$\left(\frac{\partial G}{\partial N}\right)_{T,p} = \left(\frac{\partial}{\partial N} N\varphi(T,p)\right)_{T,p} = \varphi(T,p) = \mu$$

Therefore,

$$G(T,p,N) = N\mu(T,p). \quad \text{QED}$$

(Note: this argument works only because G depends on <u>only one</u> extensive quantity N. For $F(T,V,N)$ both V and N are extensive so $F(T,V,N) \neq N\varphi(T,V)$.)

For a system with n different species, we can generalize the expressions for G:

$$G(T,p,N_1 \ldots N_n) = \sum_{i=1}^{n} N_i \mu_i(T,p)$$

$$dG = -SdT + Vdp + \sum_{i=1}^{n} \mu_i dN_i \text{ where } \mu_i = \left(\frac{\partial G}{\partial N_i}\right)_{T,p,N_{j\neq i}}$$

These relations will be very useful for understanding chemical reactions and chemical equilibrium.

KEY CONCEPT: <u>chemical equilibrium</u>
Chemical reactions usually are under conditions of constant p and T, so G is the appropriate thermodynamic potential to use. At equilibrium G is minimized.

Ex: consider the reaction called "nitrogen fixation":
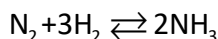
$$N_2 + 3H_2 \rightleftarrows 2NH_3$$

Puts nitrogen in a form that can be used by plants to synthesize amino acids, etc.

We can write this as an equation:

$$-1 \cdot N_2 - 3 \cdot H_2 + 2 \cdot NH_3 = 0$$

by convention, reactants are negative and products are positive.

In general we can write any chemical reaction as

$$v_1 \cdot A_1 + v_2 \cdot A_2 + \cdots v_n \cdot A_n = \sum_{i=1}^{n} v_i \cdot A_i = 0$$

where A_i is the ith chemical species

At constant p, T and equilibrium:

$$dG = 0 = -\cancel{S dT} + \cancel{V dp} + \sum_{i=1}^{n} \mu_i dN_i$$

dN_i are the changes in the number of molecules of species i during the reaction.

The chemical reaction let's us relate the different dN_i. If we write $d\hat{N}$ = the number of reaction cycles, then for the nitrogen fixation reaction:

$$dN_{N_2} = -1 \cdot d\hat{N} \qquad dN_{H_2} = -3 \cdot d\hat{N} \qquad dN_{NH_3} = +2 \cdot d\hat{N}$$

For the nitrogen fixation reaction: $-\mu_{N_2} - 3\mu_{H_2} + 2\mu_{NH_3} = 0$. (Note: we can think of this equality as a condition of diffusive equilibrium between a system of reactants and a system of products).

In general, $dN_i = v_i \cdot d\hat{N}$ and the equilibrium condition is:

$$\mu_1 \cdot v_1 + \mu_2 \cdot v_2 + \cdots \mu_n \cdot v_n = \sum_{i=1}^{n} \mu_i \cdot v_i = 0$$

Treating N_2, H_2 and NH_3 as ideal gases (with $p_i = n_i k_B T$):

$$\mu_i = k_B T \ln \frac{n_i}{n_Q} = k_B T \ln \frac{p_i}{n_Q k_B T} = \mu_i^0 + k_B T \ln \frac{p_i}{p_0}$$

p_i is called the partial pressure, the hypothetical pressure of that gas i if it alone occupied the volume of the system (i.e. $p_{tot} = p_{N_2} + p_{H_2} + p_{NH_3}$). In the last step, we conventionally write the chemical potential relative to some standard state (usually atmospheric pressure, p_0 = 1 atm).

$$-\mu_{N_2}^0 - k_B T \ln \frac{p_{N_2}}{p_0} - 3\mu_{H_2}^0 - 3k_B T \ln \frac{p_{H_2}}{p_0} + 2\mu_{NH_3}^0 + 2k_B T \ln \frac{p_{NH_3}}{p_0} = 0$$

$$k_B T \ln \left(\frac{p_{N_2} p_{H_2}^3}{p_{NH_3}^2 p_0^2} \right) = \underbrace{-\mu_{N_2}^0 - 3\mu_{H_2}^0 + 2\mu_{NH_3}^0}_{\Delta G^0 (T, p_0)}$$

So,

$$\frac{p_{NH_3}^2 p_0^2}{p_{N_2} p_{H_2}^3} = e^{-\Delta G^0 / k_B T} \equiv K(T) \qquad \text{"Law of mass action"}$$

ΔG^0, the standard Gibbs free energy of the reaction, and $K(T)$, the equilibrium constant, are constants depending on the particular reaction and can be found tabulated for different temperatures. They are defined such that $\Delta G^0 < 0$, $K(T) > 1$ means the reaction proceeds to the right (and vice versa).

For nitrogen fixation $\Delta G^0 = -32.9 \, \text{kJ/mol}$:

$$K(T) = \exp \left(\frac{+32.9 \times 10^3 \, \text{J/mol}}{6 \times 10^{23} \text{mol}^{-1} \cdot 1.38 \times 10^{-23} \, \text{J/K} \cdot 298\text{K}} \right) = 5.9 \times 10^5$$

Equation shows that if we increase double the amount of the reactants $p_{N_2} \to 2p_{N_2}$ and $p_{H_2} \to 2p_{H_2}$, the amount of product quadruples $p_{NH_3} \to 4p_{NH_3}$. Increasing the total pressure $p_{tot} = p_{H_2} + p_{N_2} + p_{NH_3}$ leads to much more NH_3 being produced.

Question 3: Consider chemical reaction below. a) Write down the equilibrium condition for the chemical potentials, and b) corresponding law of mass action:
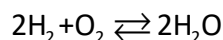
$$2H_2 + O_2 \rightleftarrows 2H_2O$$

a) The reaction can be written as the equation $-2 \cdot H_2 - 1 \cdot O_2 + 2 \cdot H_2O = 0$, so

$$-2\mu_{H_2} - \mu_{O_2} + 2\mu_{H_2O} = 0$$

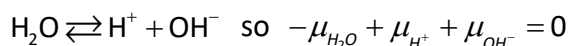b) Substituting for the chemical potentials:

$$k_B T \ln\left(\frac{p_{H_2}^2 p_{O_2}}{p_{H_2O}^2 p_0}\right) = \underbrace{-2\mu_{H_2}^0 - \mu_{O_2}^0 + 2\mu_{H_2O}^0}_{\Delta G^0(T, p_0)}$$

$$\frac{p_{H_2O}^2 p_0}{p_{H_2}^2 p_{O_2}} = e^{-\Delta G^0/k_B T} = K(T)$$

This formalism also works for dilute solutions: $\mu_i = \mu_i^0 + k_B T \ln \frac{n_i}{n_0}$

where n_i is the concentration of solute, usually measured in molars = M = mol/L, and n_0 is a standard reference concentration, usually n_0 = 1 M.

Ex: dissociation of water

$$H_2O \rightleftarrows H^+ + OH^- \quad \text{so} \quad -\mu_{H_2O} + \mu_{H^+} + \mu_{OH^-} = 0$$

It turns out that for water $\mu_{H_2O} \approx \mu_{H_2O}^0$ so,

$$k_B T \ln\frac{[H^+][OH^-]}{n_0^2} = -\mu_{H_2O}^0 + \mu_{H^+}^0 + \mu_{OH^-}^0, \text{ where } [H^+] \equiv n_{H^+} \text{ and } [OH^-] \equiv n_{OH^-}$$

$$[H^+][OH^-] = n_0^2 e^{-\Delta G^0/k_B T} = n_0^2 K(T)$$

For water $K = 10^{-14}$. When all H^+ and OH^- come from H_2O, then

$$[H^+] = [OH^-] = 10^{-7} M$$

Define <u>pH</u> as: $pH = -\log_{10}[H^+]$

For pure water pH = 7. When other substances are dissolved in water, they can add H^+ or OH^-:
For an "acidic" solution pH < 7 (i.e. $[H^+] > 10^{-7} M$)
For a "basic" solution pH > 7 (i.e. $[OH^-] > 10^{-7} M$)