

PART XII

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- 1) Chemical potential
- 2) Generalization of the 1st law of thermodynamics to systems with variable number of particles.
- 3) Example: variation of entropy at mixture
- 4) Chemical potentials of solute and solvent.
- 5) Example: freezing temperature of salt water
- 6) Phase equilibrium in a multi-component system. Gibbs phase rule

Consider a uniform system consisting of particles of one type

$$\mu(p, T) = \frac{1}{N} G(p, T) \Rightarrow G = N \mu(p, T)$$

↑
Gibbs free energy per particle (sometimes per mole).

$dg = -s dt + v dp$ - 1st law. This assumes that $N = \text{const}$.

Consider now N as an independent variable. \Rightarrow

$$dg = \left(\frac{\partial g}{\partial T} \right)_{p, N} dT + \left(\frac{\partial g}{\partial p} \right)_{T, N} dp + \left(\frac{\partial g}{\partial N} \right)_{T, p} dN \Rightarrow$$

$$\Rightarrow \boxed{dg = -s dt + v dp + \mu dN}$$

$$\begin{cases} F = G - pV \\ H = G + TS \\ U = G + TS - pV \end{cases}$$

This gives

$$\begin{aligned} dG &= -SdT + vdp + \mu dN \\ dF &= -SdT - pdv + \mu dN \\ dH &= Tds + vdp + \mu dN \\ dU &= Tds - pdv + \mu dN \end{aligned}$$

1st law of thermodynamics for a system with variable number of particles.

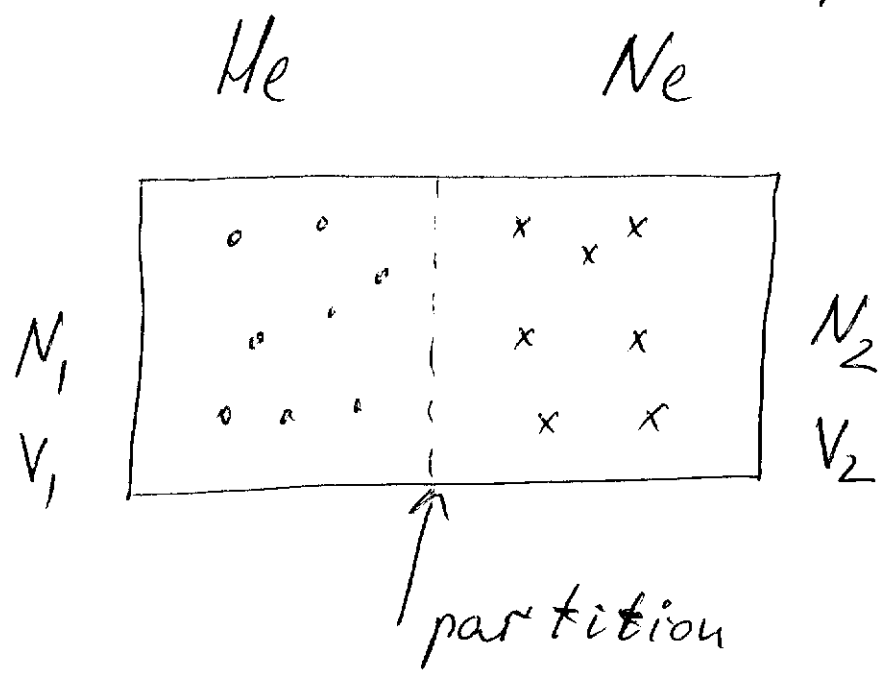
Generalization to a multi-component system (uniform)

$$\begin{cases} \mu dN \rightarrow \mu_1 dN_1 + \mu_2 dN_2 + \dots \\ \mu_i = \left(\frac{\partial G}{\partial N_i} \right)_{p, T, N_j \neq N_i} \end{cases}$$

Example: air

- 1) - O_2
- 2) CO_2
- 3) H_2O
-

Example: variation of entropy at mixture of two ideal gases



initial state with partition

pressures and temperatures are equal:

$$\begin{cases} p_1 = p_2 = p \\ T_1 = T_2 = T \end{cases}, \quad \begin{cases} pV_1 = N_1 kT \\ pV_2 = N_2 kT \end{cases}$$

$$g_i = N_1 \mu_{1i} + N_2 \mu_{2i}, \quad i = \text{initial.}$$

For an ideal gas the Gibbs free energy per mole is

$$g = RT [\ln p + \varphi(T)] - \text{see page } \underline{\underline{137}}$$

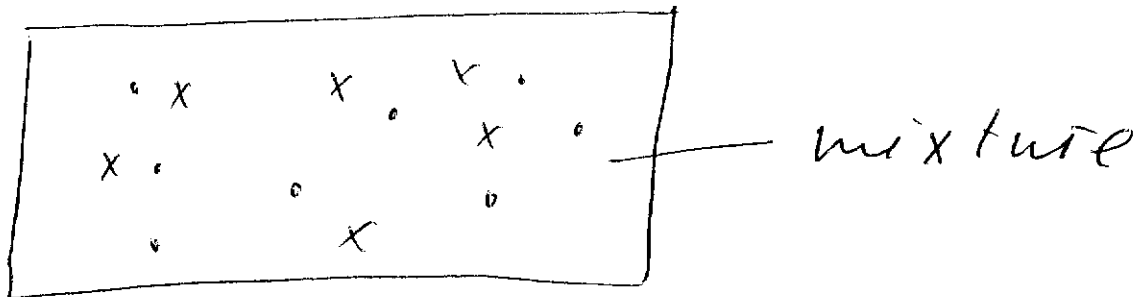
of the notes

Therefore $\mu = kT [\ln p + \varphi(T)]$

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$$G_i = N_1 kT (\ln p + \varphi_1) + N_2 kT (\ln p + \varphi_2)$$

Final state; remove partition



U is not changed $\Rightarrow T$ is not change.

$p(V_1 + V_2) = (N_1 + N_2)kT \Rightarrow p$ is not change.

However now $p = p_1 + p_2$, where p_i is a partial pressure

$$p_1(V_1 + V_2) = N_1 kT \Rightarrow \frac{p_1}{p} = \frac{N_1}{N_1 + N_2}$$

$$p_2(V_1 + V_2) = N_2 kT \Rightarrow \frac{p_2}{p} = \frac{N_2}{N_1 + N_2}$$

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$$G_f = N_1 \mu_{1f} + N_2 \mu_{2f} = N_1 kT (\ln p_1 + \phi_1) + N_2 kT (\ln p_2 + \phi_2)$$

variation of the Gibbs free energy

$$\begin{aligned} \Delta G = G_f - G_i &= N_1 kT \ln \frac{p_1}{p} + N_2 kT \ln \frac{p_2}{p} = \\ &= N_1 kT \ln \frac{N_1}{N_1 + N_2} + N_2 kT \ln \frac{N_2}{N_1 + N_2} \end{aligned}$$

$\Delta G < 0$. This agrees with the prin
that G takes min. value
in the equilibrium at
given p and T .

Variation of entropy

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

$$\Delta S = S_f - S_i = - \frac{\partial}{\partial T} (G_f - G_i) =$$

$$= - N_1 k \ln \frac{N_1}{N_1 + N_2} - N_2 k \ln \frac{N_2}{N_1 + N_2} > 0, \text{ ok!}$$

Solutions, solute, solvent.

Continue consideration of the example with mixture of two ideal gases.

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$$G = N_1 \mu_1 + N_2 \mu_2 = N_1 kT (\ln p_1 + \phi_1) + N_2 kT (\ln p_2 + \phi_2)$$

$$p_1 = p x_1, \quad x_1 = \frac{N_1}{N_1 + N_2}$$

$$p_2 = p x_2, \quad x_2 = \frac{N_2}{N_1 + N_2}$$

concentrations

$$g = N_1 kT (\ln p + \phi_1) + N_1 kT \ln x_1 +$$

$$+ N_2 kT (\ln p + \phi_2) + N_2 kT \ln x_2$$

Let us check that $\mu_i = \frac{\partial g}{\partial N_i}$

$$? \mu_1 = \frac{\partial g}{\partial N_1} = \underbrace{kT (\ln p + \phi_1) + kT \ln x_1}_{= \mu_1} +$$

$$+ N_1 kT \frac{\partial}{\partial N_1} \ln x_1 + N_2 kT \frac{\partial}{\partial N_1} \ln x_2 =$$

$$= \mu_1 + N_1 kT \frac{\partial}{\partial N_1} \left(\ln \frac{N_1}{N_1 + N_2} \right) + N_2 kT \frac{\partial}{\partial N_1} \ln \frac{N_2}{N_1 + N_2}$$

$$= \mu_1 + N_1 kT \left(\frac{1}{N_1} - \frac{1}{N_1 + N_2} \right) + N_2 kT \left(-\frac{1}{N_1 + N_2} \right) =$$

$$= \mu_1, \quad \text{OK!}$$

Consider now the case $x_2 \ll 1$, $x_1 \approx 1$

$$g = N_1 kT (\ln p + \phi_1(T)) + N_1 kT \ln \frac{N_1}{N_1 + N_2} +$$

$$+ N_2 kT (\ln p + \phi_2(T)) + N_2 kT \ln \frac{N_2}{N_1 + N_2}$$

$\approx x_2$

$$\rightarrow \ln \frac{N_1}{N_1 + N_2} = \ln \left(1 - \frac{N_2}{N_1 + N_2} \right) \approx 1 - x_2$$

$$g \approx N_1 kT (\ln p + \phi_1(T)) +$$

$$+ N_2 kT [\ln p + \phi_2(T) - 1] + N_2 kT \ln x_2$$

Consider this as a series in powers of N_2 : There is a term independent of N_2 , a term $N_2 kT \ln x_2$, a term linear in N_2 , and we neglect higher powers of N_2 .

Consider now a general solution:
real gas, liquid or even solid.

$N_1 \rightarrow N$ - number of molecules of solvent

$N_2 \rightarrow n$ - number of molecules of solute

$$X = \frac{n}{N} \ll 1$$

The Gibbs free energy of the solution.

$$G(N, n, p, T) = N\mu_0(p, T) + N\psi(p, T) + nKT \ln X$$

Series in powers of n

- 1) $\mu_0(p, T)$ is the chemical potential of the pure solvent.
- 2) $\psi(p, T)$ is some function of p and T .
- 3) An important lesson of the previous "ideal gas" example is that there is $nKT \ln X = nKT \ln \frac{n}{N}$ term.

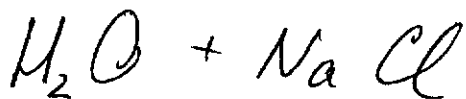
Chemical potential of the solvent:

$$\mu_1 = \frac{\partial G}{\partial N} = \mu_0 - kT \frac{n}{N} = \mu_0 - kT X$$

Chemical potential of the solute:

$$\mu_2 = \frac{\partial G}{\partial n} = kT \ln X + (kT + \psi) = kT \ln X + \tilde{\psi}(p, T)$$

Example: freezing temperature of salt water.



X_1 - concentration of salt in water.
 In the ice the salt is not soluted,
 hence $X_{ice} = 0$

Condition of phase equilibrium

$$\mu_{H_2O}^{(ice)} = \mu_{H_2O}^{(water)}$$

For $\mu_{H_2O}^{(water)}$ see eq. at page 176

$$\mu_{H_2O}^{(w)} = \mu_0^{(w)} - kTX$$

$$\mu_0^{(i)}(p, T) = \mu_0^{(w)}(p, T) - kTX$$

with salt

$$\mu_0^{(i)}(p, T_0) = \mu_0^{(w)}(p, T_0)$$

no salt

$T_0 = 0^\circ C \approx 273 K$ - freezing point

Take difference:

$$\mu_0^{(i)}(p, T) - \mu_0^{(i)}(p, T_0) = \mu_0^{(w)}(p, T) - \mu_0^{(w)}(p, T_0) - kTX$$

$$\Rightarrow \frac{\partial \mu_0^{(i)}}{\partial T} \Delta T = \frac{\partial \mu_0^{(w)}}{\partial T} \Delta T - kTX$$

$\tilde{s} = - \left(\frac{\partial \mu_0}{\partial T} \right)_p$ - entropy per H_2O molecule

$$k T X = (\tilde{s}^{(i)} - \tilde{s}^{(w)}) \Delta T = - \frac{\tilde{l}_{12}}{T} \Delta T$$

$\tilde{l}_{12} = T (\tilde{s}^{(w)} - \tilde{s}^{(i)})$ - heat of melting per molecule.

$R = k N_A$ hence

$$\Delta T = - \frac{R T^2 X}{\tilde{l}_{12}}$$

\tilde{l}_{12} is the heat of melting per mole; $\tilde{l}_{12} = N_A l_{12} \approx 6 \cdot 10^6$ Joule

Ocean (average):

$$\frac{m_{NaCl}}{m_{H_2O}} = 34.8 \cdot 10^{-3} \Rightarrow X = 34.8 \cdot 10^{-3} \cdot \frac{18}{58} = 10.8 \cdot 10^{-3}$$

$H_2O \rightarrow 18$ - molecular weight

$^{11}Na^{17}Cl \rightarrow 58$ - molecular weight

$$\Delta T = - \frac{8.31 \cdot 10^3}{6 \cdot 10^6} (273)^2 \cdot 10.8 \cdot 10^{-3} = -1.7^\circ \text{C} \quad (179)$$

"Experiment": $\Delta T \approx -1.9^\circ \text{C}$

Phase equilibrium in a multi-component system (no chemical reactions!)
Gibbs phase rule.

$i = 1, 2, 3, \dots, K$ - constituent

For example:

$i=1$	- water	H_2O
$i=2$	- Oxygen	O_2
$i=3$	- Salt	NaCl

$j = 1, 2, 3, \dots, \pi$ - phase

For example:

$j=1$	- solid
$j=2$	- liquid
$j=3$	- gas

Equations of phase equilibrium: (180)

$\mu_i^{(j)}$ - chemical potential

$$i=1 (H_2O): \mu_1^{(1)} = \mu_1^{(2)} = \dots = \mu_1^{(\pi)}$$

$$i=2 (O_2): \mu_2^{(1)} = \mu_2^{(2)} = \dots = \mu_2^{(\pi)}$$

$$i=3 (NaCl): \mu_3^{(1)} = \mu_3^{(2)} = \dots = \mu_3^{(\pi)}$$

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Altogether we have $N_e = k(\pi - 1)$ equations

Number of independent variables:

P, T + $(k-1)$ concentrations in each phase.

Altogether

there are $N_v = \pi(k-1) + 2$

independent variables.

f is the excess of the number of variables over the number of equations

$$f = N_v - N_e \quad f \text{ is called variance.}$$

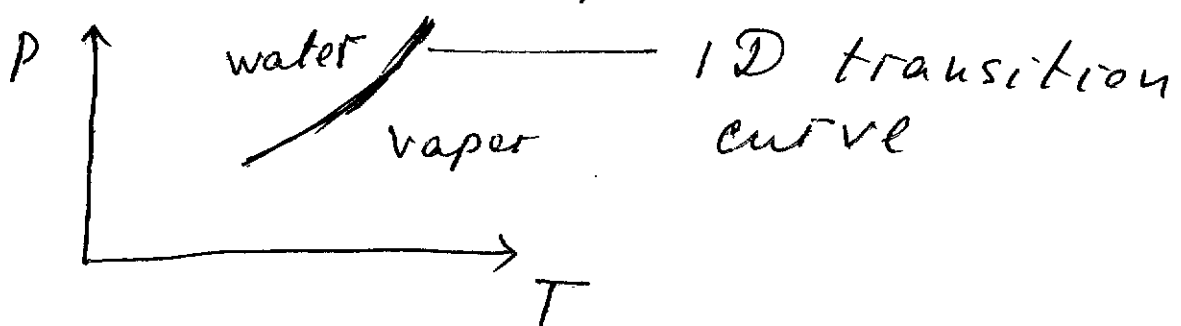
$$f = N_v - N_e = \pi(k-1) + 2 - k(\pi-1) = k - \pi + 2$$

$$f = k - \pi + 2 \quad - \text{Gibbs phase rule.}$$

Examples

1) water in equilibrium with vapor

$$\pi = 2, k = 1 \Rightarrow f = 1$$



2) Triple point: $\pi = 3, k = 1, \Rightarrow f = 0$

