

Gibbs free energy

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So far we have considered thermal and diffusive contact. Now we will consider mechanical contact.

★ In thermal contact, energy is exchanged

In thermal equilibrium, temperature is constant/
shared T

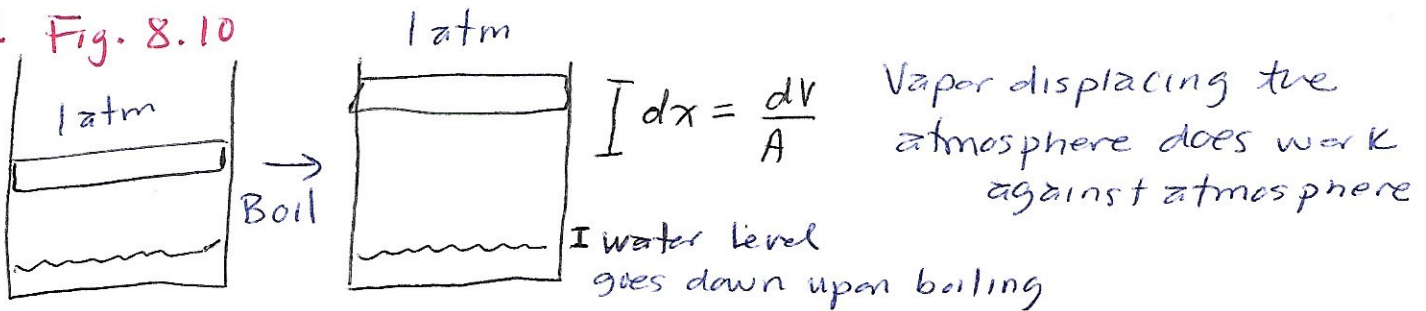
★ In diffusive contact, particles are exchanged

In diffusive equilibrium, chemical potential is constant/
shared μ

★ In mechanical contact, volume is exchanged

In mechanical equilibrium, pressure is constant/shared P

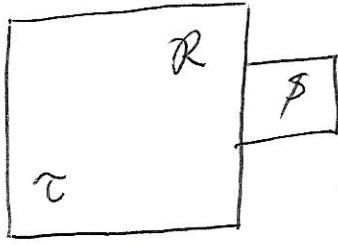
KK Fig. 8.10



A process that occurs at constant pressure is called isobaric. They are particularly important because most experiments and processes of importance are isobaric.

Consider a system in thermodynamic equilibrium with a reservoir. The first law of thermodynamics:

$$dW = dU - dQ = dU - d(\tau \sigma) \\ = dU - \tau d\sigma - \sigma d\tau$$



★ If the process is isothermal, $d\tau = 0$, so

$dW = dU - \tau d\sigma = dF$ **KK Eq. 8.36**
 $\{ F \text{ is the Helmholtz free energy}$

$\{ dQ \equiv \tau d\sigma \text{ is the heat received by the system}$

★ If work is done on the system without heat transfer, so $dQ = 0$, $dW = dU$ All the work goes towards increasing the internal energy

★ If there is a heat transfer but no work is done, so $dW = 0$, $0 = dU - dQ \Rightarrow dQ = dU$ All the heat goes towards increasing the internal energy

★ If work is done on the system and there is a heat transfer, but temperature is constant $dW = dF$ **change in Helmholtz free energy is work done isothermally**

Now consider a system also in mechanical equilibrium with a reservoir. The mechanical work:

$$-d(pV) = -pdV - Vdp \quad \text{done by or against the atmosphere}$$

★ If the process is isobaric, $dp = 0$, so $-d(pV) = -pdV$

In the case of thermal equilibrium, some energy gets "trapped" in maintaining the temperature, so the Helmholtz free energy describes the energy available for useful work.

★ In the case of mechanical equilibrium, some work has to be done against the atmosphere. This work is not available for other purposes, so the effective work is

$$dW' = dW + d(pV)$$

$$dW' = dU - dQ + d(pV) \quad \text{KK Eq. 8.37}$$

$$\text{Let } H = U + pV \Rightarrow dH = dU + d(pV) \quad \text{KK Eq. 8.38}$$

$$dW' = dH - dQ$$

H is called the enthalpy. It has ~~the same~~, at constant pressure, the same role that the internal energy U has at constant volume.

★ if no effective work is done, then $dW' = 0 = dH - dQ$

$$\Rightarrow dH = dQ$$

All the heat goes towards increasing the enthalpy. This describes, e.g., the vaporization of a liquid from an open vessel. Heat of vaporization is the enthalpy difference between the liquid and gas phases

If effective work is done, pressure is constant, and temperature is constant

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$$dW' = dU - \tau d\sigma + d(pV)$$

$$dW' = dF + d(pV) \quad \text{KK Eq. 8.39}$$

$$\text{Let } G = F + pV \Rightarrow dG = dF + d(pV) \quad \text{KK Eq. 8.40}$$

$$\text{so } dW' = dG$$

G is called the Gibbs free energy.

The Helmholtz free energy is ^{internal} energy minus energy required to maintain the temperature.

The Gibbs free energy is the internal energy minus energy required to maintain the temperature and energy required to maintain the pressure.

Chemists call the Gibbs free energy the "free energy" just like physicists call the Helmholtz free energy the "free energy."

In chemical reactions, typically the volume changes as the reaction occurs at atmospheric pressure and constant temp.

Chemical work

Work performed by the transfer of particles to a system is called chemical work because it is associated with the chemical potential. Recall the thermodynamic

$$\text{identity } dU = \tau d\sigma - p dV + \mu dN \quad \text{KK Eq. 8.49}$$

since $dU = dW' + \tau d\sigma - p dV$,

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$$\tau d\sigma - p dV + \mu dN = dW' + \tau d\sigma - p dV$$

~~$\mu dN = dW'$~~

since $dW' = dW + p dV$,

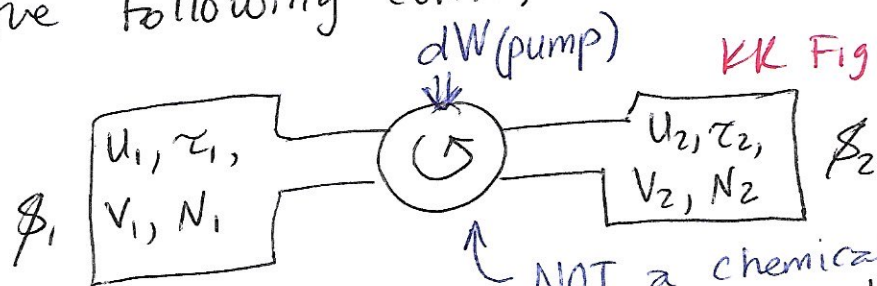
$$\mu dN = dW + p dV$$

$$\Rightarrow dW = \underbrace{-p dV}_{\text{mechanical work}} + \underbrace{\mu dN}_{\text{chemical work}}$$

KK Eq. 8.50

$$dW_c = \mu dN \quad \text{KK Eq. 8.51}$$

If there is no volume change, $dV=0$, so all the work is chemical work. Consider two systems β_1 and β_2 in the following configuration:



KK Fig. 8.14

The total chemical work $dW_c = dW_{c1} + dW_{c2} = \mu_1 dN_1 + \mu_2 dN_2$

Let $dN = dN_2 = -dN_1$, then $dW_c = -\mu_1 dN + \mu_2 dN$

This provides another meaning of $dW_c = (\mu_2 - \mu_1) dN$ KK Eq. 8.52

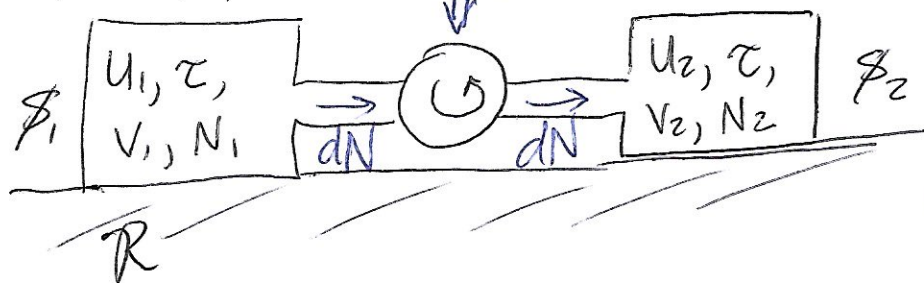
the chemical potential: the difference in chemical potential between two substances is the work required to move one particle from one system to the other.

Example: chemical work for an ideal gas

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$$n_1 = N_1/V_1$$

$$n_2 = N_2/V_2$$



connected to R , so
isothermal

Let $n_2 > n_1$ and $dV=0$

The chemical potential for an ideal gas is $\mu = \tau \ln n$,

$$\text{so } \mu_2 - \mu_1 = \tau \left[\ln \left(\frac{n_2}{n_0} \right) - \ln \left(\frac{n_1}{n_0} \right) \right] = \tau \ln (n_2/n_1) \quad \text{KK Eq. 8.53}$$

$$\int dW_c = \int (\mu_2 - \mu_1) dN = \tau \ln (n_2/n_1) \int dN = N \tau \ln (n_2/n_1)$$

Also, $pV = N\tau$

$$W = - \int_{V_1}^{V_2} p dV = -N\tau \int_{V_1}^{V_2} \frac{dV}{V} = -N\tau \ln V \Big|_{V_1}^{V_2} = -N\tau [\ln V_2 - \ln V_1]$$

$$W = N\tau \ln (V_1/V_2) = N\tau \ln (n_2/n_1) \quad \text{KK Eq. 8.54}$$

This illustrates the equivalence of the different types of work