

# HH0027 Free Energies and Work in Different Forms

Unlike heat, work can appear in different forms. For instance, consider a system with internal energy  $U = U(\sigma, V, N)$

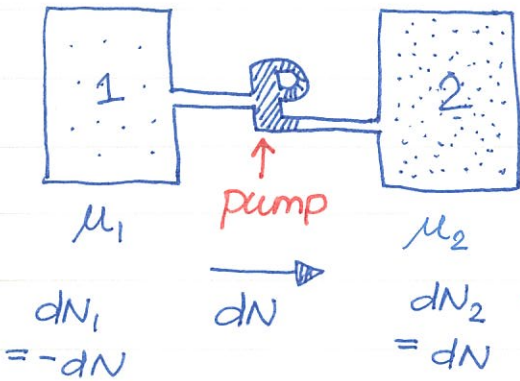
$$dU = \left(\frac{\partial U}{\partial \sigma}\right)_{V,N} d\sigma + \left(\frac{\partial U}{\partial V}\right)_{\sigma,N} dV + \left(\frac{\partial U}{\partial N}\right)_{\sigma,V} dN$$

work, because  $\sigma = \text{constant!}$

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

In the above expression,  $-pdV$  is mechanical work and  $\mu dN$  is chemical work.

$dW_c = \mu dN$

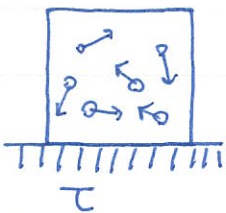


To transfer a particle from system 1 to system 2 requires some chemical work  $dW_c$

$$dW_c = dW_q + dW_c = \mu_1 dn_1 + \mu_2 dn_2 = (\mu_2 - \mu_1) dN$$

Although internal energy is great for conceptual understanding, in realistic situations, various free energies are convenient.

## ⊙ Isothermal work:



For a system at constant temperature  $\tau$ , the 1<sup>st</sup> law can be written as,

$$dU = dQ + dW = \underline{d(\tau\sigma)} + dW$$

total differential

Introduce the Helmholtz free energy

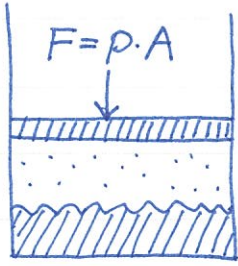
$F = U - \tau\sigma$



$dF = dW$

a convenient form of the 1<sup>st</sup> law.

### ① Isobaric work:



Consider a boiling liquid at constant pressure. The mechanical work is  $dW_m = -pdV = -d(pV)$ . It's inspiring to rewrite the 1<sup>st</sup> law as

$$dU = dQ + dW = dQ + dW_{\text{eff}} + dW_m$$

$$\rightarrow \underline{d(U + pV) = dQ + dW_{\text{eff}}} \quad \leftarrow \text{other forms of work, except the mechanical.}$$

It's convenient to introduce another free energy called enthalpy

$$\boxed{H \equiv U + pV} \quad \rightarrow \quad \boxed{dH = dQ + dW_{\text{eff}}} \quad \leftarrow \text{the 1<sup>st</sup> law again!}$$

### ② Isothermal and Isobaric work:

What about a thermal process at constant  $\tau$  and  $p$ ? Most chemical reactions occur under this situation. Let's rewrite the 1<sup>st</sup> law again:  $dU = dQ + dW = d(\tau\sigma) + dW_{\text{eff}} - d(pV)$

$$\rightarrow \underline{d(U - \tau\sigma + pV) = dW_{\text{eff}}} \quad \leftarrow \text{other forms of work, except the mechanical one.}$$

Introduce the Gibbs free energy

$$\boxed{G \equiv U - \tau\sigma + pV} \quad \rightarrow \quad \boxed{dG = dW_{\text{eff}}}$$

☺ Comments: In above, I tried to motivate the emergence of different free energies from the 1<sup>st</sup> law. They can also be understood by the Legendre transformation.

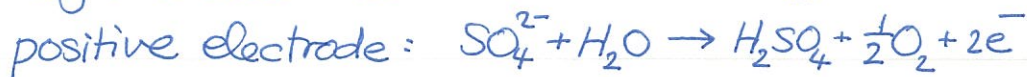
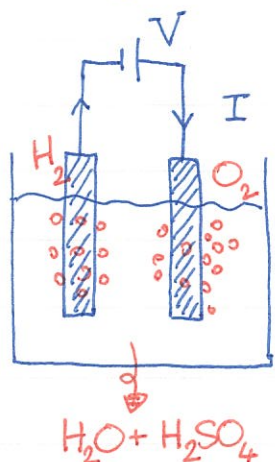
$$U = U(\sigma, \underline{V}, N) \quad \leftrightarrow \quad H = H(\sigma, \underline{p}, N) = U + pV$$

$$\left(\frac{\partial U}{\partial V}\right)_{\sigma, N} = -p \quad \leftrightarrow \quad \left(\frac{\partial H}{\partial p}\right)_{\sigma, N} = V$$

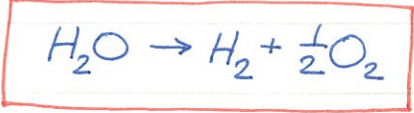
$F, G$  can also be understood this way!



Let's work on concrete examples. The first example is about electrolysis and fuel cells.



The net reaction is



Because the chemical reaction occurs at constant  $\tau$  and  $p$ , it's convenient to write the 1<sup>st</sup> law as

$$\Delta G = W_{eff} \quad W_{eff} = \Phi V = 2eN_A V_0$$

$$\Delta G = G(H_2) + \frac{1}{2}G(O_2) - G(H_2O)$$

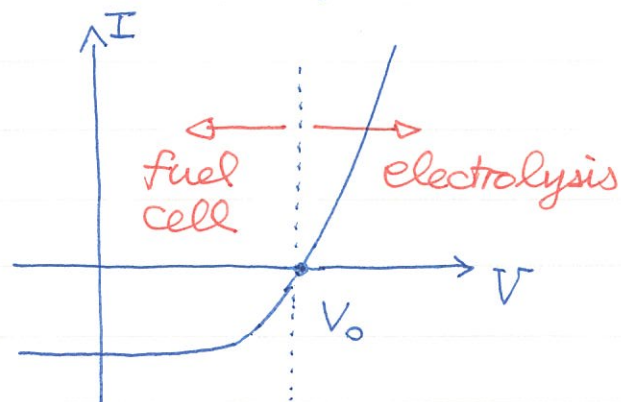
The difference of the Gibbs free energy for water decomposition is  $\Delta G = 237 \text{ kJ/mole}$ . We can estimate the voltage to

maintain electrolysis of water:

$$2eN_A V_0 = \Delta G$$

$$\rightarrow V_0 \approx 1.23 \text{ volts}$$

In realistic situation,  $V > V_0$  is OK and the extra energy dissipates as the Joule heat in the electrolyte and the circuit.

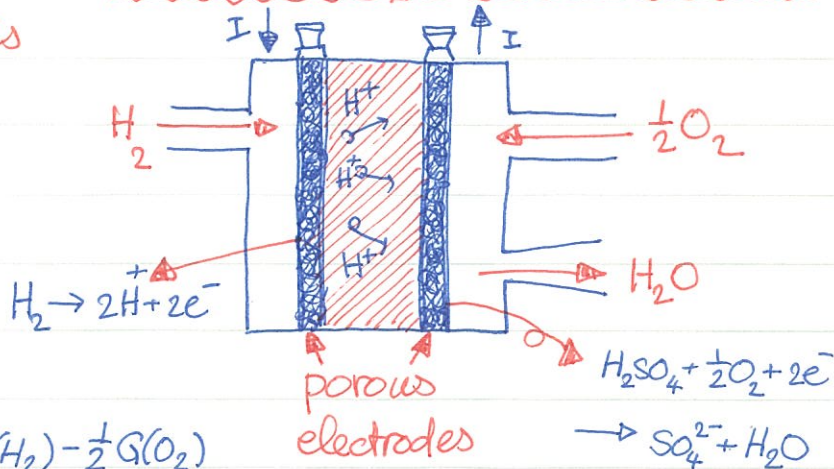


When  $V < V_0$ , it can act as a fuel cell

$$\text{because } \Delta G = G(H_2O) - G(H_2) - \frac{1}{2}G(O_2)$$

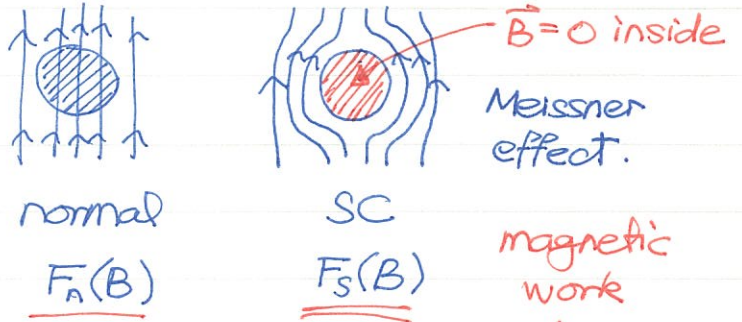
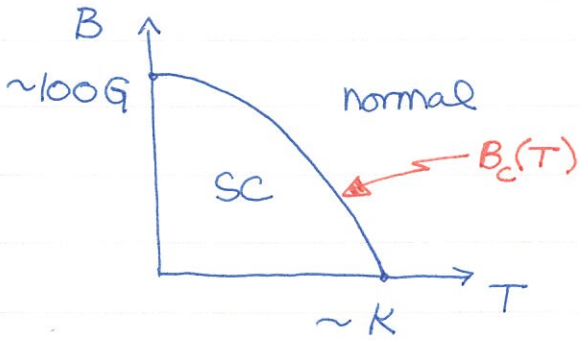
is less than zero!

Q: What happens when  $V < V_0$ ?



① Magnetic work and superconductor

Applying magnetic field on superconductors can destroy SC into the normal phase. The phase diagram for Type-I superconductor is shown here. How can we understand the critical magnetic field  $B_c(T)$ ?



We need to compare the free energies:

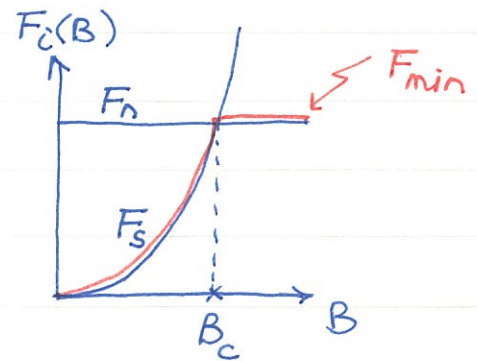
$F_n(\tau, B) \approx F_n(\tau, 0)$  and  $F_s(\tau, B) \approx F_s(\tau, 0) + \frac{B^2}{2\mu_0} \cdot V$

For  $\tau < \tau_c$ ,  $F_s(\tau, 0) < F_n(\tau, 0)$  because SC phase is stable in the absence of magnetic field.

At  $B = B_c$ ,  $F_n(\tau, B) = F_s(\tau, B)$

$F_n(\tau, 0) = F_s(\tau, 0) + \frac{B_c^2}{2\mu_0} \cdot V$

→  $\frac{1}{V} [F_n(\tau) - F_s(\tau)] = \frac{1}{2\mu_0} B_c^2(\tau)$



As  $\tau \rightarrow \tau_c^-$ , the difference between the free energies vanishes and  $B_c(\tau) \rightarrow 0$ . For even higher temperature  $\tau > \tau_c$ ,  $F_n(\tau) < F_s(\tau)$  and the normal phase always wins at all  $B$ .



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