

## Lecture 14. More on Thermodynamic Potentials

Potential	Variables
<b><math>U(S, V, N)</math></b>	<b><math>S, V, N</math></b>
<b><math>H(S, P, N)</math></b>	<b><math>S, P, N</math></b>
<b><math>F(T, V, N)</math></b>	<b><math>V, T, N</math></b>
<b><math>G(T, P, N)</math></b>	<b><math>P, T, N</math></b>

$$dU(S, V, N) = T dS - P dV + \mu dN$$

$$dH(S, P, N) = T dS + V dP + \mu dN$$

$$dF(T, V, N) = -S dT - P dV + \mu dN$$

$$dG(T, P, N) = -S dT + V dP + \mu dN$$

Maxwell relation:  $\left( \frac{\partial T}{\partial V} \right)_{S, N} = - \left( \frac{\partial P}{\partial S} \right)_{V, N}, \dots$



# Extensive and intensive variables

Extensive variables:  $V, N, S, U, H, F, G, \dots$       Confirm this for  
Intensive variables:  $T, P, \mu$ , density, ...      monatomic ideal  
gas ↙

Recall: 
$$\left. \begin{aligned} G &= N\mu \\ G &\equiv U - TS + PV \end{aligned} \right\} \Rightarrow U(S, V, N) = TS - PV + \mu N$$

This is the integrated form of 1<sup>st</sup> law (**thermodynamic identity**).

$$\begin{aligned} dU &= TdS - PdV + \mu dN \Rightarrow \Delta U_i = T\Delta S_i - P\Delta V_i + \mu\Delta N_i \\ \Rightarrow U &= \sum_i \Delta U_i = T \sum_i \Delta S_i - P \sum_i \Delta V_i + \mu \sum_i \Delta N_i = TS - PV + \mu N \end{aligned}$$

$$\Rightarrow dU = TdS + SdT - PdV - VdP + \mu dN + Nd\mu$$

$$\Rightarrow SdT - VdP + Nd\mu = 0 \quad \text{Gibbs-Duhem equation}$$

$$d\mu = -\frac{S}{N}dT + \frac{P}{N}dV$$

# Chemical Potential of an Ideal gas

$$\mu \equiv -T \left( \frac{\partial S}{\partial N} \right)_{U,V} = \left( \frac{\partial U}{\partial N} \right)_{S,V}$$

$\mu$  has units of energy: it's an amount of energy we need to (usually) **remove** from the system after adding one particle in order to keep its total energy fixed.

**Monatomic ideal gas:**

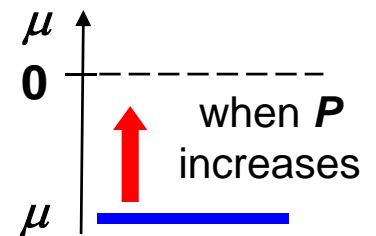
$$S(N, V, U) = N k_B \left\{ \ln \left[ V \left( \frac{4\pi m}{3h^2} U \right)^{3/2} \right] - \ln N^{5/2} + \frac{5}{2} \right\}$$

$$\mu = -T \left( \frac{\partial S}{\partial N} \right)_{U,V} = -k_B T \ln \left[ \frac{V}{N} \left( \frac{2\pi m}{h^2} k_B T \right)^{3/2} \right] = k_B T \ln \left( \frac{h^3}{(2\pi m)^{3/2}} \cdot \frac{P}{(k_B T)^{5/2}} \right)$$

At normal  $T$  and  $P$ ,  $\mu$  for an ideal gas is **negative** (e.g., for He,  $\mu \sim -5 \cdot 10^{-20} \text{ J} \sim -0.3 \text{ eV}$ ).

**Sign “-”:** by adding particles to this system, we increase its entropy. To keep  $dS = 0$ , we need to subtract some energy, thus  $\Delta U$  is negative.

The chemical potential increases with its pressure. Thus, the molecules will flow from regions of high density to regions of lower density or from regions of high pressure to those of low pressure.



Note that  $\mu$  in this case is negative because  $S$  increases with  $n$ . This is not always the case. For example, for a system of fermions at  $T \rightarrow 0$ , the entropy is zero (all the lowest states are occupied), but adding one fermion to the system costs some energy (the Fermi energy). Thus,

$$\mu(T = 0) = E_F > 0$$

# The Quantum Concentration

$$\mu = -k_B T \ln \left[ \frac{V}{N} \left( \frac{2\pi m}{h^2} k_B T \right)^{3/2} \right] = k_B T \ln \left[ n \left( \frac{h^2}{2\pi m k_B T} \right)^{3/2} \right] = k_B T \ln \left( \frac{n}{n_Q} \right)$$

where  $n=N/V$  is the concentration of particles

When  $n \ll n_Q$  (In the limit of low densities), the gas is in the classical regime, and  $\mu < 0$ .

When  $n \rightarrow n_Q$ ,  $\mu \rightarrow 0$

$$n_Q = \left( \frac{2\pi m}{h^2} k_B T \right)^{3/2}$$

- the so-called **quantum concentration** (one particle per cube of side equal to the thermal de Broglie wavelength).

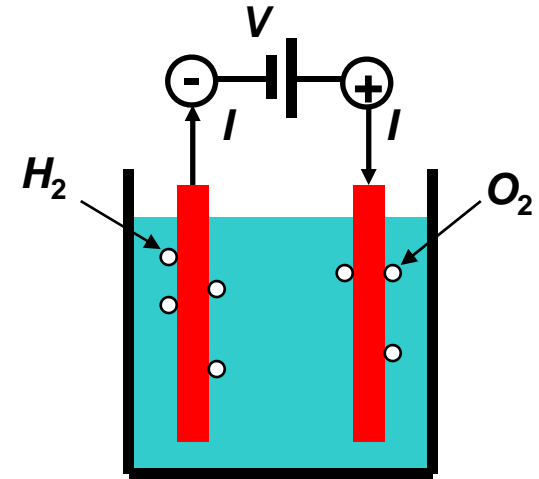
$$\lambda_{dB} = \frac{h}{p} \propto \frac{h}{\sqrt{mk_B T}} \quad n_Q = \frac{1}{\lambda_{dB}^3} \propto \left( \frac{mk_B T}{h^2} \right)^{3/2}$$

At  $T=300\text{K}$ ,  $P=10^5 \text{ Pa}$ ,  $n \ll n_Q$ . When  $n \rightarrow n_Q$ , the quantum statistics comes into play.

# Electrolysis of Water

By providing energy from a battery, water can be dissociated into the diatomic molecules of hydrogen and oxygen. Electrolysis is a (slow) process that is both **isothermal** and **isobaric** ( $P, T = \text{const}$ ).

The tank is filled with an electrolyte, e.g. dilute sulfuric acid (we need some ions to provide a current path), platinum electrodes do not react with the acid.



When  $I$  is passed through the cell,  $\text{H}^+$  move to the “-” electrode:  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

The sulfate ions move to the “+” electrode:  $\text{SO}_4^{--} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \frac{1}{2}\text{O}_2 + 2\text{e}^-$



The electrical work required to decompose 1 mole of water:  
(neglect the Joule heating of electrolyte)

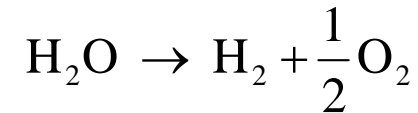
$$\Delta W_{\text{other}} = \Delta G = G(\text{H}_2) + \frac{1}{2}G(\text{O}_2) - G(\text{H}_2\text{O})$$

In the Table (p. 404), the Gibbs free energy  $\Delta G$  represents the change in  $G$  upon forming 1 mole of the material starting with elements in their **most stable** pure states:

$$\Delta G(\text{H}_2) = 0 \quad \Delta G(\text{O}_2) = 0 \quad \Delta G(\text{H}_2\text{O}) = -237 \text{ kJ/mole}$$

$$\Delta W_{\text{other}} = \Delta G = 237 \text{ kJ/mole}$$

# Electrolysis of Water (cont.)



**Convenience of G:** let's consider the same reaction, but treat it in terms of  $\Delta U$ ,  $\Delta V$ , and  $\Delta S$ :

$$\Delta W_{\text{other}} = \Delta G = \Delta U + P\Delta V - T\Delta S$$

**$P\Delta V$ :** we will neglect the initial volume of water in comparison with the final volume of gas. By dissociating 1 mole of water, we'll get 1.5 moles of gas. The work by gas:

$$\Delta W = PV = nRT = (1.5 \text{ mol})(8.3 \text{ J/mol} \cdot \text{K})(300 \text{ K}) \approx 3.7 \text{ kJ}$$

**$-T\Delta S$ :** the entropy of a mole of substance (from the same Table, p.404) –  
 $S(\text{H}_2)=130.7 \text{ J/K}$ ,  $S(\text{O}_2)=205.1 \text{ J/K}$ ,  $S(\text{H}_2\text{O})=69.9 \text{ J/K}$ ,

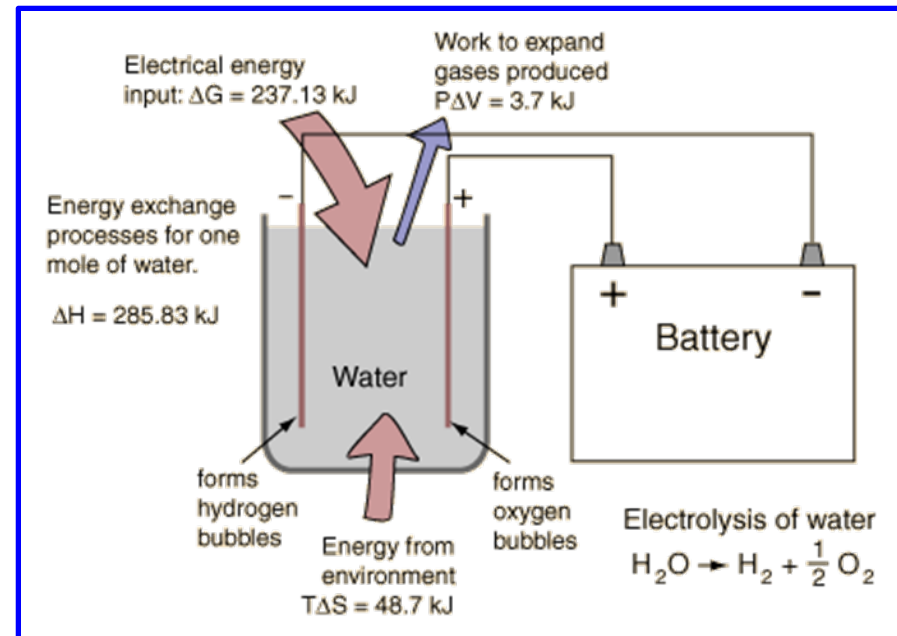
$$-T\Delta S = -(300 \text{ K})(130.7 \text{ J/K} + 0.5 \cdot 205.1 \text{ J/K} - 69.9 \text{ J/K}) \approx -49 \text{ kJ}$$

**$\Delta U$ :** ??? – not in the Table...

Well, we got  $\Delta H$  in the Table -  $\Delta H(\text{H}_2) = 0$ ,  $\Delta H(\text{O}_2) = 0$ ,  $\Delta H(\text{H}_2\text{O}) = -285.8 \text{ kJ}$  ( $\Delta H$  upon forming 1 mol of the material starting with elements in their most stable pure states).

$$\Delta G = \Delta H - T\Delta S$$

$$286 \text{ kJ} - 49 \text{ kJ} \approx 237 \text{ kJ}$$



# Electrolysis of Water (cont.)

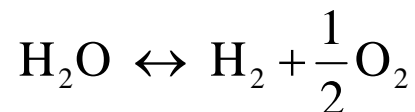
The process must provide the energy for the dissociation plus the energy to expand the produced gases. Both of those are included in  $\Delta H$ . Since the enthalpy  $H = U + PV$ , the change in internal energy  $\Delta U$  is then:

$$\Delta U = \Delta H - P\Delta V \approx 286 \text{ kJ} - 4 \text{ kJ} = 282 \text{ kJ}$$

However, it is not necessary to put in the whole amount in the form of electrical energy. Since the entropy increases in the process of dissociation, the amount  $T\Delta S$  can be provided from the environment. Since the electrolysis results in an increase in entropy, the environment “helps” the process by contributing  $T\Delta S$ .

The min. voltage required for electrolysis:

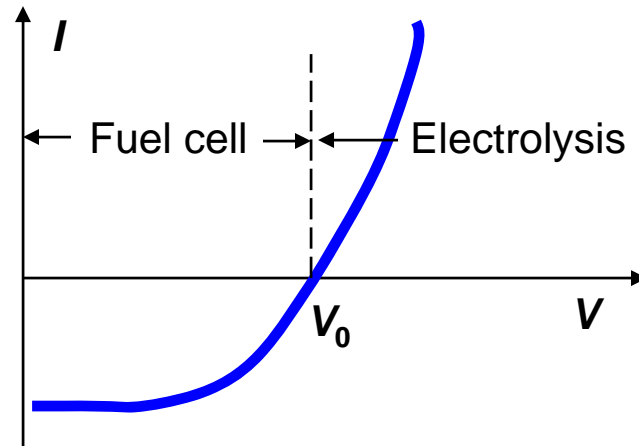
$$\Delta W^* = 237 \text{ kJ} = V \times I \times \Delta t = V \times Q = V \times (-2N_A e)$$



$$V_0 = \frac{\Delta G}{2N_A e} = \frac{2.37 \cdot 10^5 \text{ J/mole}}{1.93 \cdot 10^5 \text{ C/mole}} = 1.23 \text{ V}$$

(Pr. 5.4)

If  $V < V_0$ , the reaction will proceed from right to left provided gaseous hydrogen is available at the “+” electrode and gaseous oxygen at the “-” electrode.



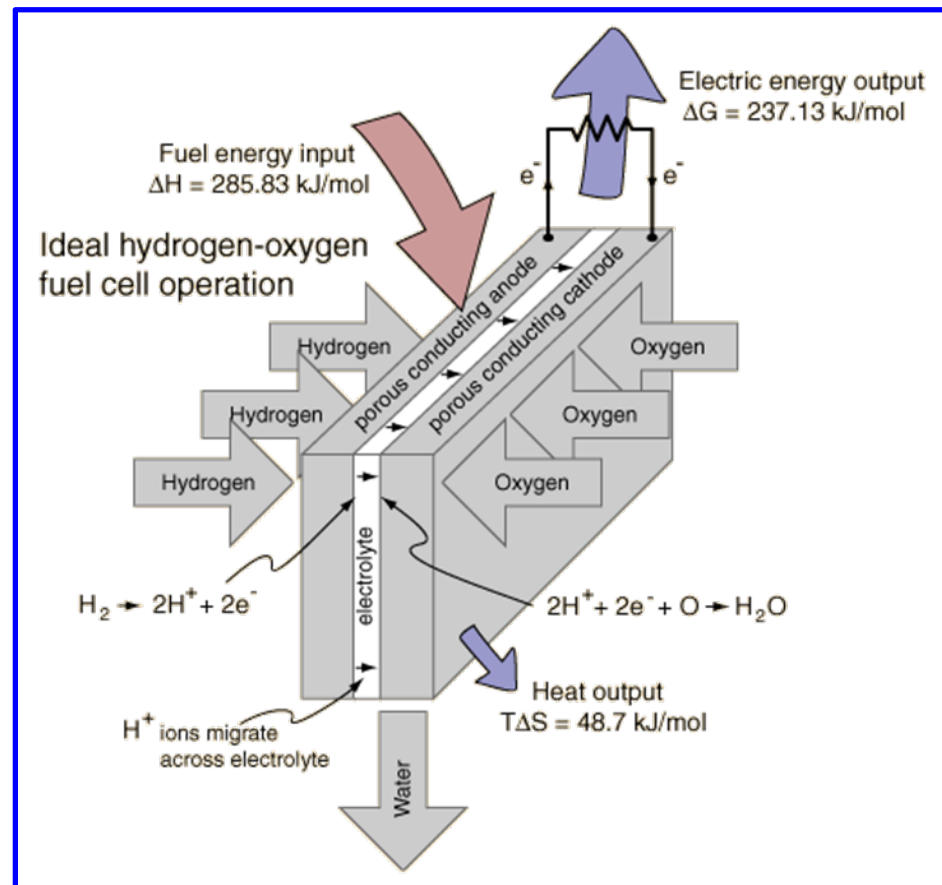
# Fuel Cells

Hydrogen and oxygen can be combined in a fuel cell to produce electrical energy. FC differs from a battery in that the fuel ( $H_2$  and  $O_2$ ) is continuously supplied.

By running the process of electrolysis in reverse (*controllable* reaction between  $H_2$  and  $O_2$ ), one can extract 237 kJ of electrical work for 1 mole of  $H_2$  consumed. The efficiency of an ideal fuel cell :

$$(237 \text{ kJ} / 286 \text{ kJ}) \times 100\% = \mathbf{83\%} !$$

This efficiency is far greater than the ideal efficiency of a heat engine that burns the hydrogen and uses the heat to power a generator.



The entropy of the gases decreases by 49 kJ/mol since the number of water molecules is less than the number of  $H_2$  and  $O_2$  molecules combining. Since the total entropy cannot decrease in the reaction, the excess entropy must be expelled to the environment as heat.



## Fuel Cell at High T

Fuel cells operate at elevated temperatures (from  $\sim 70^\circ\text{C}$  to  $\sim 600^\circ\text{C}$ ). Our estimate ignored this fact – the values of  $\Delta G$  in the Table are given at room temperature.

**Pr. 5.11**, which requires an estimate of the maximum electric work done by the cell operating at  $75^\circ\text{C}$ , shows how one can estimate  $\Delta G$  at different  $T$  by using partial derivatives of  $G$ .

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \Delta G \approx -S\Delta T$$

- these equations allow computing Gibbs free energies at non-standard  $T$  and  $P$ :

**At  $75^\circ\text{C}$  (348K):**

$$G(\text{H}_2) \approx 0 - (130 \text{ J/K})(50 \text{ K}) = -6.5 \text{ kJ}$$

$$G(\text{O}_2) \approx 0 - (205 \text{ J/K})(50 \text{ K}) = -10.25 \text{ kJ}$$

$$G(\text{H}_2\text{O}) \approx -237 \text{ kJ} - (70 \text{ J/K})(50 \text{ K}) = -240.5 \text{ kJ}$$

$$\Delta G = G(\text{H}_2\text{O}) - G(\text{H}_2) - \frac{1}{2} G(\text{O}_2) = -240.5 \text{ kJ} + 6.5 \text{ kJ} + 5.1 \text{ kJ} = -228.9 \text{ kJ}$$

Substance	$\Delta G(1\text{bar}, 298\text{K})$ kJ/mol	$S(1\text{bar}, 298\text{K})$ J/K mol
$\text{H}_2$	0	130
$\text{O}_2$	0	205
$\text{H}_2\text{O}$	-237	70

Thus, the maximum electrical work done by the cell is 229 kJ, about 3.5% less than the room-temperature value of 237 kJ. Why the difference? The reacting gases have more entropy at higher temperatures, and we must get rid of it by dumping waste heat into the environment.

# Summary

Potential	Variables
$U(S, V, N)$	$S, V, N$
$H(S, P, N)$	$S, P, N$
$F(T, V, N)$	$V, T, N$
$G(T, P, N)$	$P, T, N$

$$dU(S, V, N) = T dS - P dV + \mu dN$$

$$dH(S, P, N) = T dS + V dP + \mu dN$$

$$dF(T, V, N) = -S dT - P dV + \mu dN$$

$$dG(T, P, N) = -S dT + V dP + \mu dN$$

$$\text{Maxwell relation: } \left( \frac{\partial T}{\partial V} \right)_{S, N} = - \left( \frac{\partial P}{\partial S} \right)_{V, N}, \dots$$

$$\text{Internal energy: } U = TS - PV + \mu N \Rightarrow SdT - VdP + Nd\mu = 0$$

$$\text{Enthalpy: } H = U + PV = TS + \mu N$$

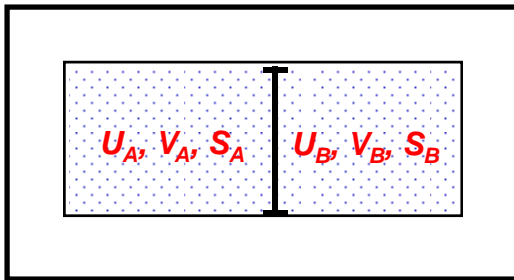
$$\text{Helmholtz Free energy: } F = U - TS = -PV + \mu N$$

$$\text{Gibbs Free energy: } G = U - TS + PV = N\mu$$

$$\text{Grand Free energy: } \Phi = U - TS - \mu N = -PV \text{ (Pr. 5.23)}$$

## Processes at $T = \text{const}$

**Problem:** Consider a cylinder separated into two parts by an adiabatic piston. Compartments **a** and **b** each contains one mole of a monatomic ideal gas, and their initial volumes are  $V_{ai}=10\text{ l}$  and  $V_{bi}=1\text{ l}$ , respectively. The cylinder, whose walls allow heat transfer only, is immersed in a large bath at  $0^\circ\text{C}$ . The piston is now moving reversibly so that the final volumes are  $V_{af}=6\text{ l}$  and  $V_{bf}=5\text{ l}$ . How much work is delivered by (or to) the system?



The process is isothermal :  $(dF)_T = (-PdV)_T$

The work delivered to the system:

$$\delta W = \delta W_a + \delta W_b = \int_{V_{ai}}^{V_{af}} dF_a + \int_{V_{bi}}^{V_{bf}} dF_b$$

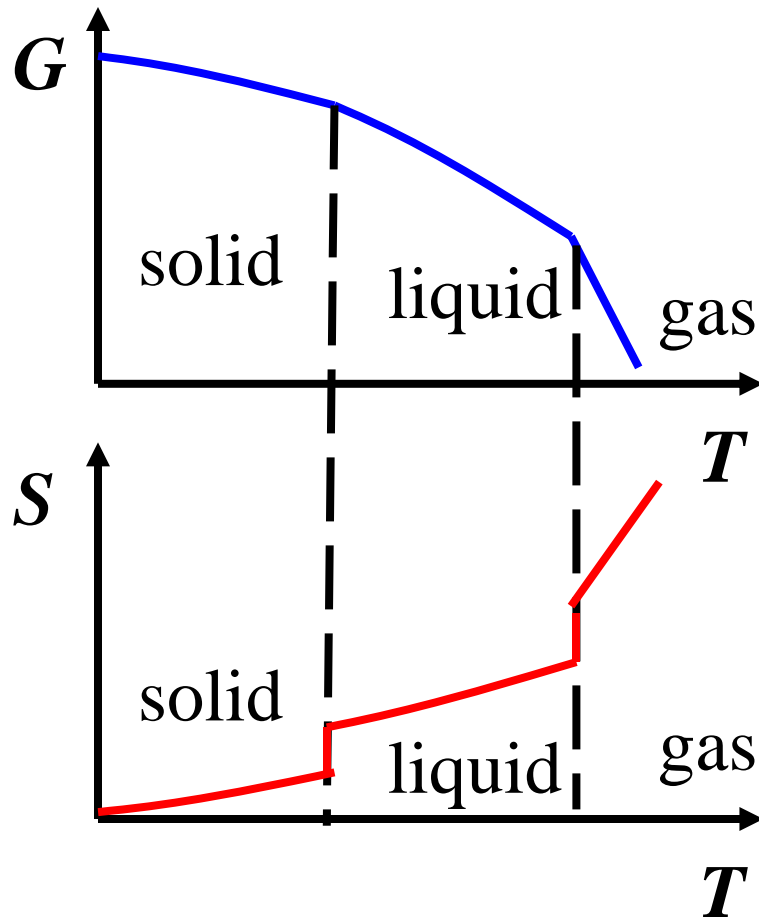
For one mole of monatomic ideal gas:

$$F = U - TS = \frac{3}{2}RT - T \cdot R \left( \ln V + \frac{3}{2} \ln T + f(N, m) \right)$$

$$\delta W = RT \ln \frac{V_{ai}}{V_{af}} + RT \ln \frac{V_{bi}}{V_{bf}} = -2.5 \times 10^3 \text{ J}$$

## Example:

**Pr.5.9.** Sketch a qualitatively accurate graph of  $G$  vs.  $T$  for a pure substance as it changes from solid to liquid to gas at fixed pressure.



$$\left( \frac{\partial G}{\partial T} \right)_P = -S \quad \Delta G \approx -S\Delta T$$

- these equations allow computing Gibbs free energies at “non-standard”  $T$  (if  $G$  is tabulated at a “standard”  $T$ )