So far, we have been using **the total internal energy U** and, sometimes, **the enthalpy H** to characterize various macroscopic systems. These functions are called the **thermodynamic potentials**: all the thermodynamic properties of the system can be found by taking partial derivatives of the TP.

For each TP, a set of so-called "natural variables" exists:

$$d\,U = T\,d\,S - P\,dV + \mu\,d\,N \qquad\qquad d\,H = T\,d\,S + V\,dP + \mu\,d\,N$$

Today we'll introduce the other two thermodynamic potentials: **the Helmhotz free energy F** and **Gibbs free energy G**. Depending on the type of a process, one of these four thermodynamic potentials provides the most convenient description (and is tabulated). All four functions have **units of energy**.

| 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* |

When considering different types of processes, we will be interested in two main issues:
- what determines the **stability** of a system and how the system evolves towards an equilibrium;
- how much work can be extracted from a system.

# Diffusive Equilibrium and Chemical Potential

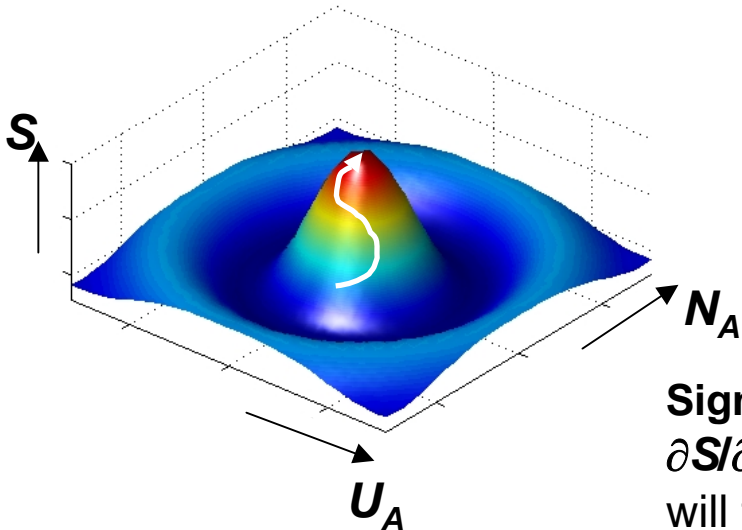For completeness, let's recall what we've learned about the chemical potential.

$$dU = TdS - PdV + \mu dN \qquad dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$$
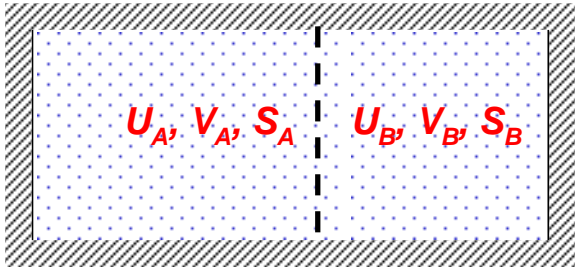
The meaning of the partial derivative $(\partial S/\partial N)_{U,V}$ : let's fix $V_A$ and $V_B$ (the membrane's position is fixed), but assume that the membrane becomes permeable for gas molecules (exchange of both $U$ and $N$ between the sub-systems, the molecules in $A$ and $B$ are the same ).

$U_A$, $V_A$, $S_A$ | $U_B$, $V_B$, $S_B$

For sub-systems in diffusive equilibrium:

$$\left(\frac{\partial S_{AB}}{\partial U_A}\right)_{V_A, N_A} = 0 \qquad \left(\frac{\partial S_{AB}}{\partial N_A}\right)_{U_A, V_A} = 0 \qquad \boxed{\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B}} \qquad \left(\frac{\partial S}{\partial N}\right)_{U,V} = -\frac{\mu}{T}$$

$$\boxed{\mu \equiv -T\left(\frac{\partial S}{\partial N}\right)_{U,V} = \left(\frac{\partial U}{\partial N}\right)_{S,V}} \qquad \text{- the chemical potential}$$

In equilibrium, $\boxed{T_A = T_B}$ $\boxed{\mu_A = \mu_B}$ $\boxed{P_A = P_B}$

**Sign "-":** out of equilibrium, the system with the larger $\partial S/\partial N$ will get more particles. In other words, particles will flow from from a high $\mu/T$ to a low $\mu/T$.

## 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:_**

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

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

At normal **T** and **P**, $\mu$ for an ideal gas is **negative** (e.g., for He, $\mu \sim - 5\cdot10^{-20}$ J $\sim - 0.3$ 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 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 .



$\mu$

**0** - - - - - - - - - -

when **P**
increases

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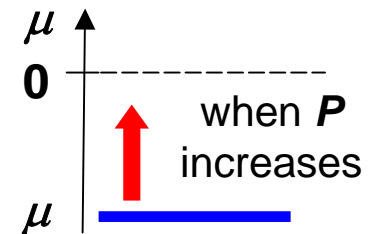
Note that $\mu$ in this case is negative because **S** increases with **n**. This is not always the case. For example, for a system of fermions at **T**→0, the entropy is zero (all the lowest states are occupied), but adding one fermion to the system costs some energy (the Fermi energy). Thus,

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

# 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** << **$n_Q$** (In the limit of low densities), the gas is in the classical regime, and μ<0.
When **n** → **$n_Q$**, μ → 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).

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

At **T**=300K, **P**=$10^5$ Pa , **n** << **$n_Q$**. When **n** → **$n_Q$**, the quantum statistics comes into play.

# Isolated Systems, independent variables *S* and *V*

Advantages of **U** : it is conserved for an **isolated** system (it also has a simple physical meaning – the sum of all the kin. and pot. energies of all the particles).

In particular, for an isolated system $\delta Q$=0, and $dU = \delta W$.

Earlier, by considering the total differential of **S** as a function of variables **U, V,** and **N,** we arrived at the thermodynamic identity for **quasistatic** processes :

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

The combination of parameters on the right side is equal to the **exact differential** of **U** . This implies that the **natural variables** of **U** are **S, V**, **N**,

Considering **S, V**, and **N** as independent variables:

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

Since these two equations for **dU** must yield the same result for any **dS** and **dV**, the corresponding coefficients must be the same:

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

Again, this shows that among several macroscopic variables that characterize the system (*P, V, T,* $\mu$, *N*, etc.), only three are independent, the other variables can be found by taking partial derivatives of the TP with respect to its natural variables.

 **Work** is the transfer of energy to a system by a change in the external parameters such as volume, magnetic and electric fields, gravitational potential, etc. We can represent $\delta W$ as the sum of two terms, a mechanical work on changing the volume of a system (an "**expansion**" work) **- PdV** and **all other kinds of work,** $\delta W_{other}$ (electrical work, work on creating the surface area, etc.):

$$\delta W = -PdV + \delta W_{other}$$

If the system comprises only solids and liquids, we can usually assume **dV $\cong$ 0**, and the difference between $\delta W$ and $\delta W_{other}$ vanishes. For gases, the difference may be very significant.

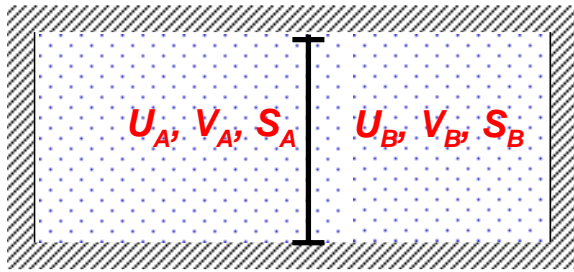initially, the system is not necessarily in equilibrium

The energy balance for an isolated system :

$$dU = T\,dS - PdV + \delta W_{other} = 0 \qquad \text{(for fixed } N)$$

$$\delta W_{other} = PdV - TdS$$

If we consider a quasi-static process (the system evolves from one equilibrium state to the other), than, since for an isolated system $\delta Q=TdS=0$,

$$\delta W_{other} = PdV$$

$U_A$, $V_A$, $S_A$ | $U_B$, $V_B$, $S_B$

For a thermally isolated system $\delta Q = 0$. If the volume is fixed, then no work gets done ($\delta W = 0$) and the internal energy is conserved:

$$U = \text{const}$$

While this constraint is always in place, the system might be out of equilibrium (e.g., we move a piston that separates two sub-systems, see Figure). If the system is initially out of equilibrium, then some **spontaneous processes will drive the system towards equilibrium**. In a state of stable equilibrium no further spontaneous processes (other than ever-present random fluctuations) can take place. The equilibrium state corresponds to the maximum multiplicity and maximum entropy. All microstates in equilibrium are equally accessible (the system is in one of these microstates with equal probability).

$$\boxed{(S)_{eq} = \max}$$

This implies that in any of these spontaneous processes, the entropy tends to increase, and the change of entropy satisfies the condition

$$dS \geq 0$$

Suppose that the system is characterized by a parameter **x** which is free to vary (e.g., the system might consist of ice and water, and **x** is the relative concentration of ice). By spontaneous processes, the system will approach the stable equilibrium (**x** = **x**$_{eq}$) where **S** attains its absolute maximum.

**S**

**x**$_{eq}$  **x**
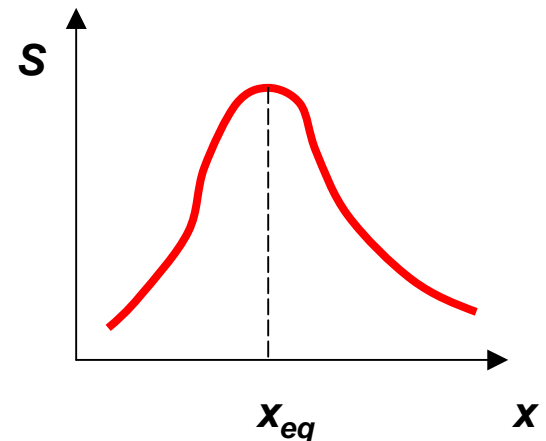
# Enthalpy (independent variables *S* and *P*)

The volume **V** is not the most convenient independent variable. In the lab, it is usually much easier to control **P** than it is to control **V**. To change the natural variables, we can use the following trick:

$$U(S,V) \rightarrow U(S,V) + PV$$



Enthalpy, *H*

Internal energy, *U*

Enthalpy and internal energy

Temperature, *T*
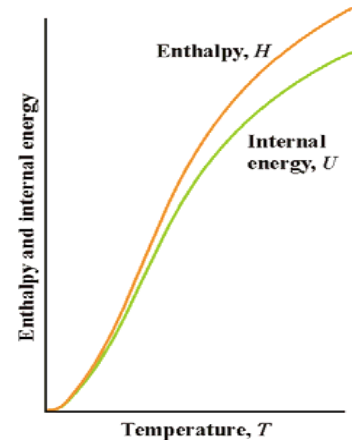
$$dH = d(U + PV) = dU + PdV + VdP \\ dU = T\,dS - PdV$$

$$dH = TdS + VdP$$

$$\boxed{dH(S,P,N) = T\,dS + VdP + \mu dN}$$

**H** (the enthalpy) is also a thermodynamic potential, with its natural variables **S**, **P**, and **N**.

- the internal energy of a system plus the work needed to make room for it at P=const.

The total differential of **H** in terms of its independent variables :

$$dH(S,P,N) = \left(\frac{\partial H}{\partial S}\right)_{P,N} dS + \left(\frac{\partial H}{\partial P}\right)_{S,N} dP + \left(\frac{\partial H}{\partial N}\right)_{S,P} dN$$

Comparison yields the relations:

$$\boxed{\left(\frac{\partial H}{\partial S}\right)_{P,N} = T \qquad \left(\frac{\partial H}{\partial P}\right)_{S,N} = V \qquad \left(\frac{\partial H}{\partial N}\right)_{S,P} = \mu}$$

In general, if we consider processes with "other" work:

$$dH = TdS + VdP + \delta W_{other}$$

For what kind of processes is **H** the most convenient thermodynamic potential?

At this point, we have to consider a system which is not isolated: it is in a thermal contact with a thermal reservoir.

$$dH = TdS + VdP + \delta W_{other} = \delta Q + VdP + \delta W_{other}$$

Let's consider the **P = const** processes with **purely "expansion" work** ($\delta W_{other} = 0$),

$$\left(dH\right)_{P,\delta W_{other}=0} = \delta Q$$

For such processes, the change of enthalpy is equal to the thermal energy ("heat") received by a system.

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$$

For the processes with **P = const** and $\delta W_{other} = $ **0**, the enthalpy plays the same part as the internal energy for the processes with **V = const** and $\delta W_{other} = $ **0.**

***Example***: the evaporation of liquid from an open vessel is such a process, because no effective work is done. The heat of vaporization is the enthalpy difference between the vapor phase and the liquid phase.

# Systems in Contact with a Thermal Reservoir

When we consider systems in contact with a large thermal reservoir (a "thermal bath, there are two complications: (a) the energy in the system is no longer fixed (it may flow between the system and reservoir), and (b) in order to investigate the stability of an equilibrium, we need to consider the entropy of the combined system (= the system of interest+the reservoir) – according to the 2$^{nd}$ Law, this total entropy should be maximized.

What should be the system's behavior in order *to maximize the total entropy*?

For the systems in contact with a eat bath, we need to invent a better, more useful approach. The entropy, along with *V* and *N*, determines the system's energy *U =U (S,V,N*). Among the three variable, the entropy is the most difficult to control (the entropy-meters do not exist!). For an isolated system, we have to work with the entropy – it cannot be replaced with some other function. And we did not want to do this so far – after all, our approach to thermodynamics was based on this concept. However, for systems in thermal contact with a reservoir, we can replace the entropy with another, more-convenient-to-work-with function.  This, of course, does not mean that we can get rid of entropy. We will be able to work with a different "energy-like" thermodynamic potential for which entropy is not one of the natural variables.

# Helmholtz Free Energy (independ. variables *T* and *V*)

Let's do the trick (Legendre transformation) again, now to exclude **S** :

$$U(S,V) \rightarrow U(S,V) - T\,S \qquad \boxed{F \equiv U - T\,S} \qquad \textbf{\textit{Helmholtz free energy}}$$

$$d(U - TS) = TdS - PdV - SdT - TdS = -SdT - PdV \qquad \boxed{dF(T,V,N) = -SdT - PdV + \mu dN}$$

The natural variables for **F** are **T, V, N:** $dF(T,V,N) = \left(\dfrac{\partial F}{\partial T}\right)_{V,N} dT + \left(\dfrac{\partial F}{\partial V}\right)_{T,N} dV + \left(\dfrac{\partial F}{\partial N}\right)_{T,V} dN$

Comparison yields the relations: $\boxed{\left(\dfrac{\partial F}{\partial T}\right)_{V,N} = -S \qquad \left(\dfrac{\partial F}{\partial V}\right)_{T,N} = -P \qquad \left(\dfrac{\partial F}{\partial N}\right)_{T,V} = \mu}$

$\left(\dfrac{\partial F}{\partial V}\right)_{T,N} = -P$ can be rewritten as: $P = -\left(\dfrac{\partial F}{\partial V}\right)_{T,N} = -\left(\dfrac{\partial U}{\partial V}\right)_{T,N} + T\left(\dfrac{\partial S}{\partial V}\right)_{T,N}$

The first term – the "energy" pressure – is dominant in most solids, the second term – the "entropy" pressure – is dominant in gases. (For an ideal gas, **U** does not depend on **V**, and only the second term survives).

**F** is the total energy needed to create the system, minus the heat we can get "**for free**" from the environment at temperature **T**. If we annihilate the system, we can't recover all its **U** as work, because we have to dispose its entropy at a non-zero **T** by dumping some heat into the environment.

# The Minimum Free Energy Principle ($V, T$ = const)

The total energy of the combined system (= the system of interest+the reservoir) is $U = U_R + U_s$, this energy is to be shared between the reservoir and the system (we assume that $V$ and $N$ for all the systems are fixed). Sharing is controlled by the maximum entropy principle:

$$S_{R+s}(U_R, U_s) = S_R(U - U_s) + S_s(U_s) \rightarrow \max$$

Since $U \sim U_R \gg U_s$

system's parameters only

$$S_{R+s}(U, U_s) = S_R(U) + \left(\frac{\partial S_R}{\partial U}\right)(-U_s) + S_s(U_s) = S_R(U) - \left[\frac{U_s}{T} - S_s\right] = S_R(U) - \frac{F_s}{T}$$

$S_{R+s}$

**reservoir +system**
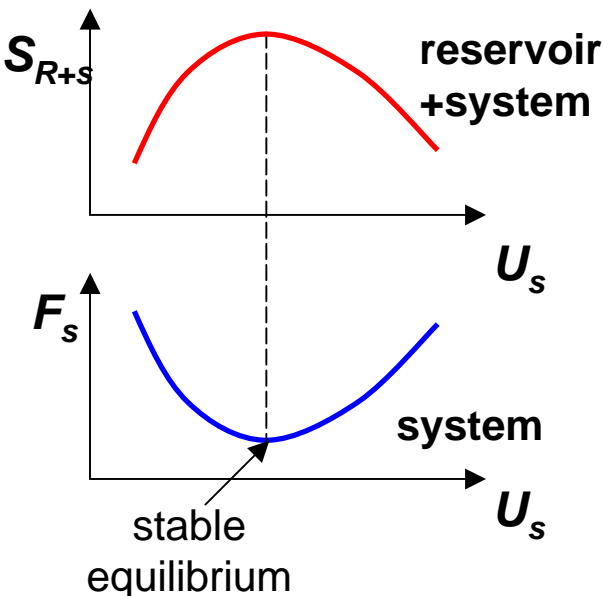
loss in $S_R$ due to transferring $U_s$ to the system

gain in $S_s$ due to transferring $U_s$ to the system

$U_s$

$F_s$

$$dS_{R+s}(U, U_s) = dS_s - \frac{dU_s}{T} = -\frac{1}{T}[dU_s - TdS_s] = -\frac{dF_s}{T}$$

**system**

$U_s$

stable equilibrium

Thus, we can enforce the **maximum** entropy principle by simply **minimizing** the Helmholtz free energy of the system without having to know anything about the reservoir except that it maintains a fixed $T$! Under these conditions (fixed $T$, $V$, and $N$), **the maximum entropy principle of an isolated system is transformed into a minimum Helmholtz free energy principle for a system in thermal contact with the thermal bath**.

# Processes at $T = \text{const}$
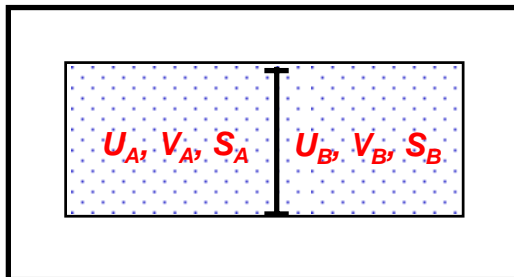
In general, if we consider processes with "other" work: $\boxed{dF = -SdT - PdV + \delta W_{other}}$

For the processes at $T$ = **const**
(in thermal equilibrium with a large reservoir): $(dF)_T = (-PdV + \delta W_{other})_T$

The **total** work performed on a system at $T$ = **const** in a **reversible** process is equal to the change in the Helmholtz free energy of the system. In other words, for the $T$ = **const** processes the Helmholtz free energy gives all the reversible work.

**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 $V_{ai}=10l$ and $V_{bi}=1l$, respectively. The cylinder, whose walls allow heat transfer only, is immersed in a large bath at $0^0C$. The piston is now moving reversibly so that the final volumes are $V_{af}=6l$ and $V_{bi}=5l$. How much work is delivered by (or to) the system?

| $U_A, V_A, S_A$ | $U_B, V_B, S_B$ |
|---|---|

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

The work delivered by 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:
$$F = U - TS = \frac{3}{2}RT - \left(\frac{3}{2}RT\ln\frac{T}{T_0} - RT\ln\frac{V}{V_0} + Tf(N,m)\right)$$

$$\delta W = RT\ln\frac{V_{af}}{V_{ai}} + RT\ln\frac{V_{bf}}{V_{bi}} = 2.6\cdot10^3 \text{ J}$$

Let's do the trick of Legendre transformation again, now to exclude both **S** and **V**:

$$U(S,V) \rightarrow U(T,P) - TS + PV$$

$$\boxed{G \equiv U - TS + PV}$$  -  the thermodynamic potential **G** is called the **Gibbs free energy**.

Let's rewrite **dU** in terms of independent variables **T** and **P**:

$$dU = TdS - PdV = d(TS) - SdT - d(PV) + VdP \qquad d(U - TS + PV) = -SdT + VdP$$

$$\boxed{dG(T,P,N) = -SdT + VdP + \mu dN}$$

Considering **T, P,** and **N** as independent variables:

$$dG(T,P,N) = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \left(\frac{\partial G}{\partial N}\right)_{T,P} dN$$

Comparison yields the relations: 

$$\boxed{\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S \qquad \left(\frac{\partial G}{\partial P}\right)_{T,N} = V \qquad \left(\frac{\partial G}{\partial N}\right)_{T,P} = \mu}$$

# Gibbs Free Energy and Chemical Potential

Combining $U = T\,S - PV + \mu N$ with $G \equiv U - T\,S + PV$ $\Rightarrow$ $\boxed{G = N\mu}$

- this gives us a new interpretation of the chemical potential: at least for the systems with only one type of particles, ***the chemical potential is just the Gibbs free energy per particle.***

The chemical potential
$$\boxed{\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}}$$

If we add one particle to a system, holding **T** and **P** fixed, the Gibbs free energy of the system will increase by $\mu$. By adding more particles, we do not change the value of $\mu$ since we do not change the density: $\mu \neq \mu(N)$.

Note that **U**, **H**, and **F**, whose differentials also have the term $\mu d\mathbf{N}$, depend on **N** ***non-linearly***, because in the processes with the independent variables (**S,V,N**), (**S,P,N**), and (**V,T,N**), $\mu = \mu(N)$ might vary with **N**.

**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.

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S$$

- the slope of the graph **G**(**T** ) at fixed **P** should be −**S**. Thus, the slope is always negative, and becomes steeper as T and S increases. When a substance undergoes a phase transformation, its entropy increases abruptly, so the slope of **G**(**T** ) is discontinuous at the transition.
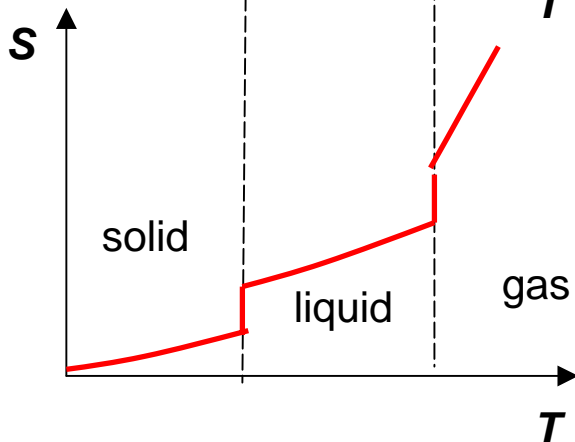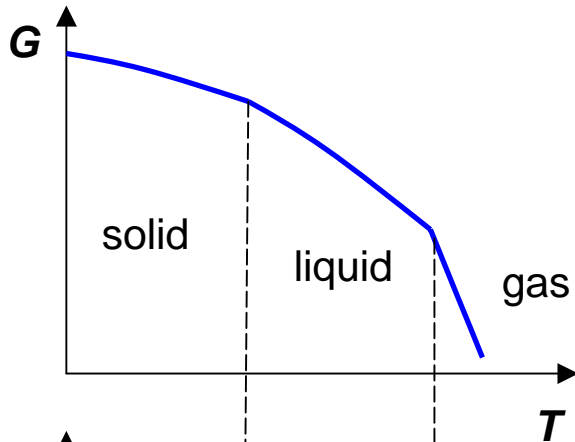


$$\left(\frac{\partial G}{\partial T}\right)_{P} = -S \quad \Delta G \approx -S\Delta T$$

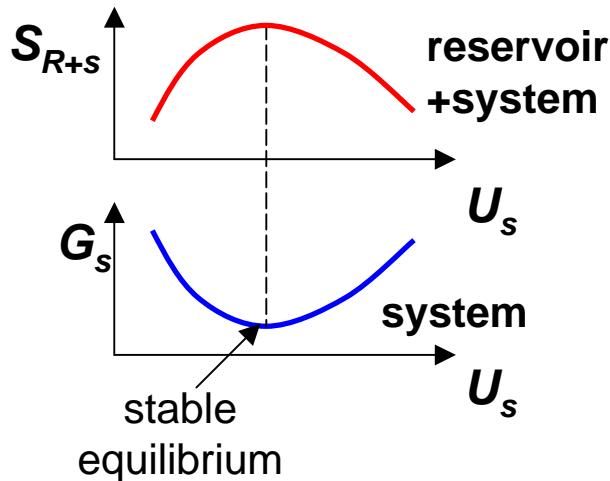- these equations allow computing Gibbs free energies at "non-standard" **T** (if **G** is tabulated at a "standard" **T**)

# The Minimum Free Energy Principle ($P, T$ = const)

The total energy of the combined system (=the system of interest+the reservoir) is $U = U_R + U_s$, this energy is to be shared between the reservoir and the system (we assume that $P$ and $N$ for all the systems are fixed). Sharing is controlled by the maximum entropy principle:

$$S_{R+s}(U_R, U_s) = S_R(U - U_s) + S_s(U_s) \rightarrow \max$$

$$dS_{R+s}(U, U_s) = dS_s - \frac{dU_s}{T} - \frac{P}{V}dV_s = -\frac{1}{T}[dU_s - TdS_s + PdV_s] = -\frac{dG_s}{T}$$



**reservoir +system**

$U_s$

**system**

$U_s$

stable equilibrium

Thus, we can enforce the maximum entropy principle by simply minimizing the Gibbs free energy of the system without having to know anything about the reservoir except that it maintains a fixed $T$! Under these conditions (fixed $P$, $V$, and $N$), **the maximum entropy principle of an isolated system is transformed into a minimum Gibbs free energy principle for a system in the thermal contact + mechanical equilibrium with the reservoir.**

$$\boxed{(dG)_{T,P,N} \leq 0}$$

Thus, if a system, whose parameters $T, P,$ and $N$ are fixed, is in thermal contact with a heat reservoir, the stable equilibrium is characterized by the condition:

$$\boxed{G = \min}$$

$G/T$ is the net entropy cost that the reservoir pays for allowing the system to have volume $V$ and energy $U$, which is why minimizing it maximizes the total entropy of the whole combined system.

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

Let's consider the processes at **P = const** and **T = const** in general, including the processes with "other" work:

$$\delta W = -PdV + \delta W_{other}$$

Then

$$dG = d(U - TS + PV)_{T,P} = (\delta Q - PdV + \delta W_{other})_{T,P} - TdS + PdV$$

$$= (\delta Q)_{T,P} + (\delta W_{other})_{T,P} - TdS = (\delta W_{other})_{T,P}$$

The "other" work performed on a system at **T = const** and **P = const** in a *reversible* process is equal to the change in the Gibbs free energy of the system.

In other words, the Gibbs free energy gives all the reversible work except the **PV** work. If the mechanical work is the only kind of work performed by a system, the Gibbs free energy is conserved: **dG = 0.**

### Gibbs Free Energy and the Spontaneity of Chemical Reactions

The Gibbs free energy is particularly useful when we consider the chemical reactions at constant **P** and **T**, but the volume changes as the reaction proceeds. *ΔG* associated with a chemical reaction is a useful indicator of weather the reaction will proceed spontaneously. Since the change in **G** is equal to the maximum "useful" work which can be accomplished by the reaction, then a *negative ΔG* indicates that *the reaction can happen spontaneously.* On the other hand, if *ΔG* is positive, we need to supply the minimum "other" work δ $W_{other}$= *ΔG* to make the reaction go.

# 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 ($P, T$ = 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.

Dissociation: $H_2SO_4 \leftrightarrow 2H^+ + SO_4^{--}$
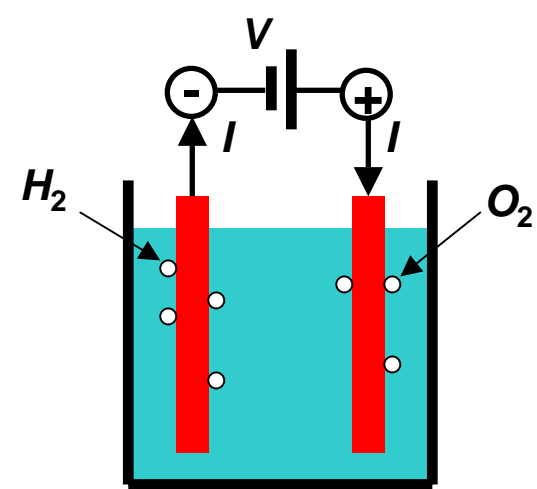
When **I** is passed through the cell, H$^+$ move to the "-" electrode: $2H^+ + 2e^- \rightarrow H_2$

The sulfate ions move to the "+" electrode: $SO_4^{--} + H_2O \rightarrow H_2SO_4 + \frac{1}{2}O_2 + 2e^-$

The sum of the above steps: $H_2O \rightarrow H_2 + \frac{1}{2}O_2$

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

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

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

$$\Delta G(H_2) = 0 \qquad \Delta G(O_2) = 0 \qquad \Delta G(H_2O) = -237 \text{ kJ/mole}$$

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

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2$$
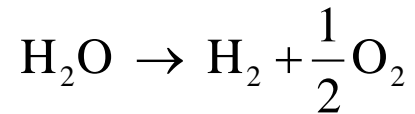
***Convenience of G***: let's consider the same reaction, but treat it in terms of $\Delta U$, $\Delta V$, and $\Delta S$:

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

$P\Delta V$: 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) – $S(H_2)$=130.7 J/K, $S(O_2)$=205.1 J/K, $S(H_2O)$=69.9 J/K,
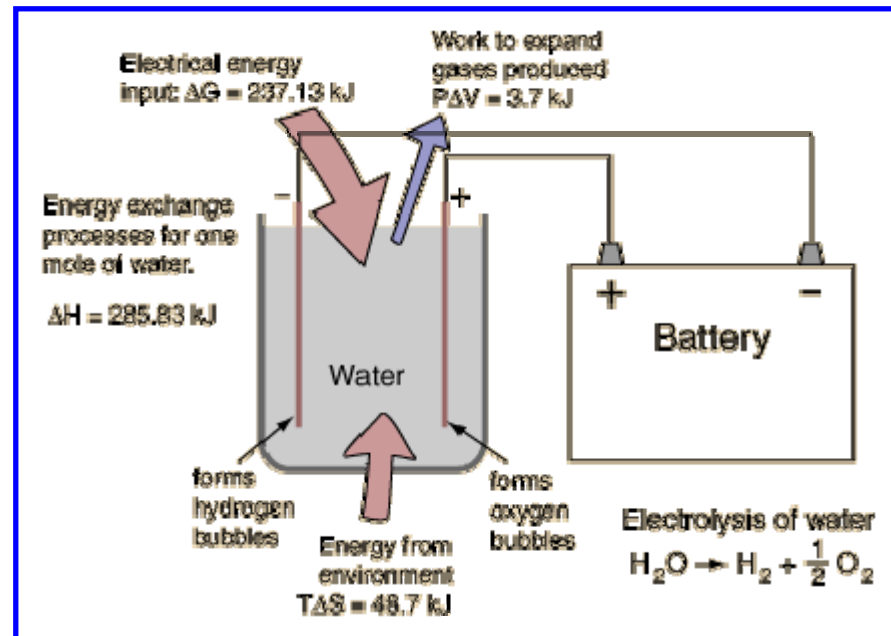
$$-T\Delta S = -(300\,\text{K})(130.7\,\text{J/K} + 0.5\cdot 205.1\,\text{J/K} - 69.9\,\text{J/K}) \approx -49\,\text{kJ}$$

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

Well, we got $\Delta H$ in the Table - $\Delta H(H_2)$ = 0, $\Delta H(O_2)$ = 0, $\Delta H(H_2O)$= - 285.8 kJ ($\Delta H$ upon forming 1 mol of the material starting with elements in their most stable pure states).



Electrical energy input $\Delta G$ = 237.13 kJ

Work to expand gases produced $P\Delta V$ = 3.7 kJ

Energy exchange processes for one mole of water.

$\Delta H$ = 285.83 kJ

Water

forms hydrogen bubbles

forms oxygen bubbles

Energy from environment $T\Delta S$ = 48.7 kJ

Battery

Electrolysis of water $H_2O \rightarrow H_2 + \frac{1}{2}O_2$

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

286 kJ  -  49 kJ  $\approx$  237 kJ

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 $T\Delta S$.
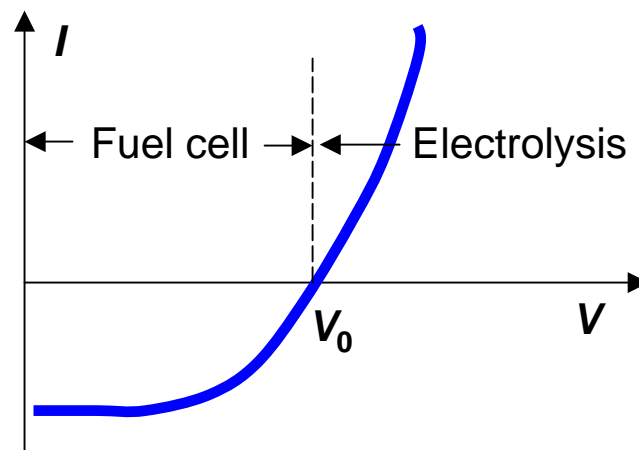
The min. voltage required for electrolysis:

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

$$H_2O \leftrightarrow H_2 + \frac{1}{2}O_2$$
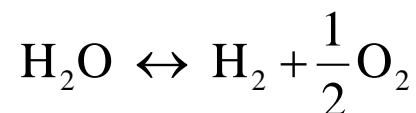
$$V_0 = \frac{\Delta G}{2N_A e} = \frac{2.37 \cdot 10^5 \text{ J/mole}}{1.93 \cdot 10^5 \text{ C/mole}} = 1.23 \text{ V}$$

(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.
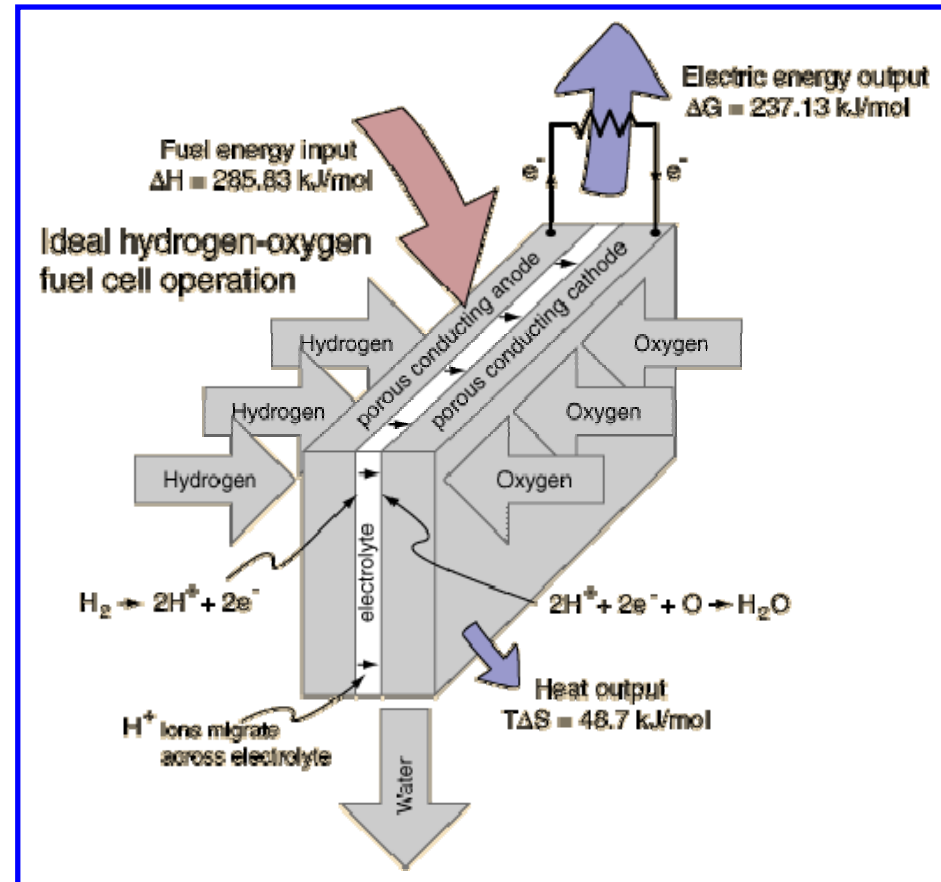
# Fuel Cells

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 kJ / 286 kJ)x100% = **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.



Ideal hydrogen-oxygen fuel cell operation

Electric energy output
$\Delta G$ = 237.13 kJ/mol

Fuel energy input
$\Delta H$ = 285.83 kJ/mol

Hydrogen / Oxygen

porous conducting anode / porous conducting cathode

$H_2 \rightarrow 2H^+ + 2e^-$

$2H^+ + 2e^- + O \rightarrow H_2O$

electrolyte

$H^+$ ions migrate across electrolyte

Heat output
$T\Delta S$ = 48.7 kJ/mol

Water

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 ~70$^0$C to ~600$^0$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$^0$C, shows how one can estimate $\Delta\boldsymbol{G}$ at different $\boldsymbol{T}$ by using partial derivatives of $\boldsymbol{G}$.

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

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

**At 75$^0$C (348K):**

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

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

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

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

| Substance | $\Delta$G(1bar, 298K) kJ/mol | S(1bar, 298K) J/K mol |
|---|---|---|
| H$_2$ | 0 | 130 |
| O$_2$ | 0 | 205 |
| H$_2$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.

# Conclusion:

| 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** |

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

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

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

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