Thermodynamic Potentials: U and H a recap

$dU = \text{đ}Q_{in} - dW_{out}$ First Law

$\boxed{dU = T\,dS - p\,dV}$ Second Law

① So the "natural variables" to describe U are S and V, $U(S,V)$:

We have

$$☆ \qquad dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

Comparing to ☆ we find

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

② For constant volume processes: $dU_V = \underset{\nwarrow\; T\,dS_V}{\text{đ}Q_V} = C_V\,dT$

So we find

$$\Delta U = \int C_V\,dT \qquad \text{or} \qquad C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\Delta S = \int \frac{C_V}{T}\,dT$$

Definitions of Thermodynamic Potentials

Function of state		Differential	Natural variables	First derivatives	
Internal energy	U	$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$	$U = U(S, V)$	$T = \left(\frac{\partial U}{\partial S}\right)_V,$	$p = -\left(\frac{\partial U}{\partial V}\right)_S$
Enthalpy	$H = U + pV$	$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p$	$H = H(S, p)$	$T = \left(\frac{\partial H}{\partial S}\right)_p,$	$V = \left(\frac{\partial H}{\partial p}\right)_S$
Helmholtz function	$F = U - TS$	$\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V$	$F = F(T, V)$	$S = -\left(\frac{\partial F}{\partial T}\right)_V,$	$p = -\left(\frac{\partial F}{\partial V}\right)_T$
Gibbs function	$G = H - TS$	$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p$	$G = G(T, p)$	$S = -\left(\frac{\partial G}{\partial T}\right)_p,$	$V = \left(\frac{\partial G}{\partial p}\right)_T$

Thermodynamic Potentials: The enthalpy H a recap

$$dU = T dS - p dV$$

Now integrate by parts $p dV = d(pV) - V dp$
So

$$dU = T dS - [d(pV) - V dp]$$

Or defining $H \equiv U + pV$ and $dH = d(U + pV)$, have:

$$\boxed{dH \equiv T\,dS + V\,dp}$$

① So the "natural variables" for H are S and p:

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dV$$

Comparing to ☆ we find

$$T = (\partial H/\partial S)_p \qquad V = (\partial H/\partial p)_S$$

② For constant pressure processes $dH_p = \overset{TdS}{\swarrow}\!\!\; dQ_p = C_p\, dT$

$$\Delta H = \int C_p\, dT \qquad \text{or} \qquad C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

$$\Delta S = \int \frac{C_p}{T}\, dT$$

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Free Energy in Thermodynamics

- Often a system is in contact with a reservoir at temperature T, and Volume V

$$\left.\begin{aligned} dU &= dQ - dW \\ dU &= T\,dS - p\,dV \end{aligned}\right\} \text{assume perfect equilibrium with reversible processes}$$

Now the temperature is fixed, so it makes sense to integrate the $T\,dS$ by parts

$$T\,dS = d(TS) - S\,dT$$

Leading to (after bringing $d(TS)$ to the LHS):

$$d(U - TS) = -S\,dT - p\,dV$$

which we identify as the Free Energy

$$\boxed{dF = -S\,dT - p\,dV} \qquad F \equiv U - TS$$

① The natural variables here are T, V, i.e. $F(T,V)$

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$$

So Comparison gives $\left(\frac{\partial F}{\partial T}\right)_V = -S$ and $\left(\frac{\partial F}{\partial V}\right)_T = -p$

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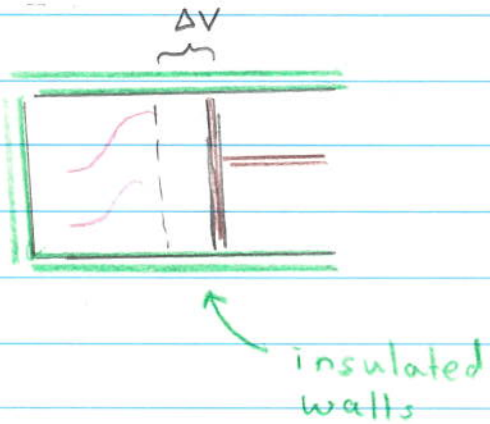
Example 1

- For a system at temperature T the reversible work done is given by $\Delta F = W_{in}$. Why is it ΔF and not ΔE?

Case 1: No heat flow S const;

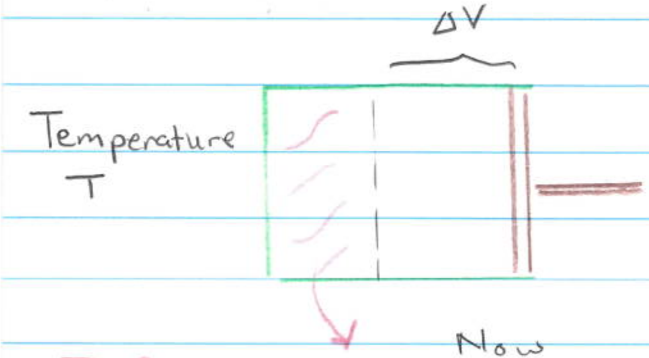


In this case no heat is exchanged with the environment

$$\Delta U = \cancelto{0}{Q} + W_{in}$$

Here $\Delta U = W_{in}$

Case 2: Const T



$-T\Delta S = Q_{out}$

In this case T is const;

$$\Delta U = \overset{T\Delta S}{Q} + W_{in}$$

$$\Delta F = \Delta U - T\Delta S = W_{in}$$

Now heat comes out as the gas is compressed at constant T;

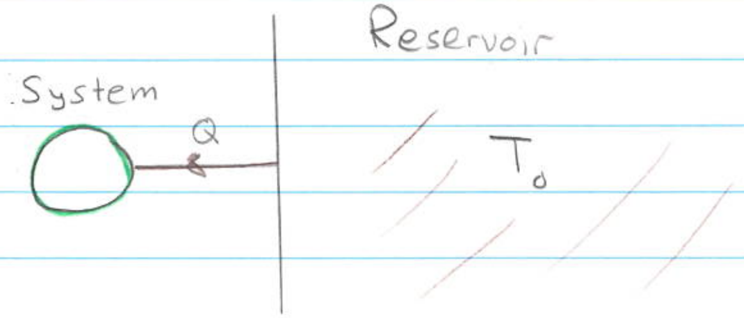
Mathematically

$$dF = -S\,\cancelto{0}{dT} - p\,dV$$

Note $V_i > V_f$

$$\Delta F = -\int_{V_i}^{V_f} \frac{NkT}{V}\,dV = +NkT \ln\left(\frac{V_i}{V_f}\right) > 0$$

Free Energy



Then the system and reservoir will evolve to maximize entropy

☆ $$dS_{sys} + dS_R \geq 0$$

The heat given to the system (and lost by the reservoir) is Q. So $dS_R = -dQ/T$

Then

☆☆ $$dS_{sys} - \frac{dQ}{T} \geq 0$$

In general $dQ = dU + dW_{out}$

$$dS_{sys} - \frac{(dU + dW_{out})}{T} \geq 0$$

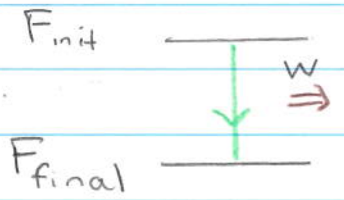
Or in terms of free energy $F = U - TS$

$$\boxed{-dF \geq dW_{out}}$$

This is the same as ☆ and ☆☆

In words:

- The work that can be extracted during any process is less than the drop in free energy. The maximum work is $W_{out}^{max} = -\Delta F$.



$$\Rightarrow -\Delta F = F_{init} - F_{final} \geqslant W_{out}$$

- Similarly the work required $W_{in} = -W_{out}$ to bring about a change in free energy is greater than $\Delta F \equiv W_{in}^{min}$, i.e. $\Delta F \le W_{in}$

- If no work is done then the system evolves to minimize its free energy

$$\boxed{\Delta F \le 0} \leftarrow$$

the system absorbs and gives heat to reservoir until F is a minimum

Example: Oxidation of Glucose

- 1 mol of Glucose $C_6H_{12}O_6$ is oxidized at NTP (25°C and 1bar) according to the reaction

$$C_6H_{12}O_6^{(s)} + 6O_2(g) \longleftrightarrow 6CO_2(g) + 6H_2O(\ell)$$

The enthalpy change is $\Delta H = -2808\ \mathrm{kJ/mol}$, with entropy change $\Delta S = +182\ \mathrm{J/°K}$. What was the change in energy and the maximum work that can be done?

① The volume change at const pressure is $\Delta V \simeq 0$ since we have 6 moles of gasses at the end and beginning. The liquids don't contribute much to δV. (See slide)

So: $\Delta U = \Delta H = -2808\ \mathrm{kJ}$

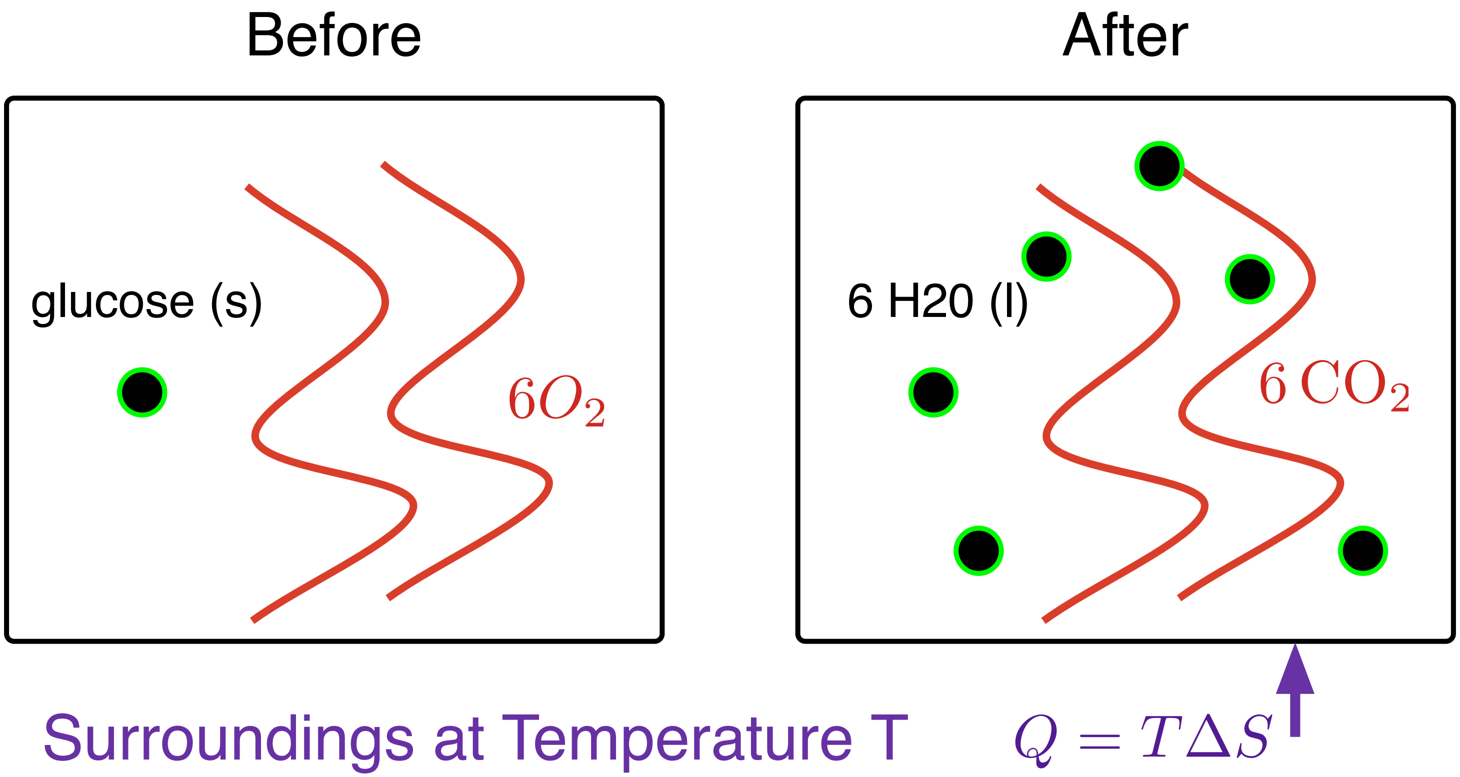
② The maximum work is

$$W_{max} = -\Delta F = -\Delta U + \underbrace{T\Delta S} = 2808\ \mathrm{kJ} + 54\ \mathrm{kJ} = 2862\ \mathrm{kJ}$$

heat coming into system from surroundings allowing more work

- The entropy change $\frac{1}{N}\frac{\Delta S}{k_B} = \frac{\Delta S}{R} = \frac{182\ \mathrm{J/°K}}{8.32\ \mathrm{J°/K}} = 22$

Oxidation of Glucose Cartoon



is positive indicating that heat will come into the system allowing the system to do more work than simply $-\Delta U$

- The ΔS is greater than zero in part because we have take a large organized molecule and broken it up into constituents which can now move in more ways, i.e. more phase space. (see slide)

- Roughly each of the 6 carbons has 4 bonds with 1eV per bond, so $24\,\text{eV} \longleftrightarrow 2400\,\text{kJ/mol} \sim \Delta H$. We used that $1 N_A \cdot (1\,\text{eV}) = 100\,\text{kJ}$. This gives an order of magnitude for ΔH

The ΔS entropy (in units of k_B) associated with the ~ 6 new degrees of freedom per glucose molecule molecule is

$$\frac{1}{6}\frac{\Delta S}{N_A k_B} = \frac{1}{6}\frac{\Delta S}{R} = \frac{22}{6} \sim 3.5$$

← This is an order 1 number as is typical.

Gibb's Free Energy

- Often a system will interact with a reservoir at fixed T and pressure p

$$\boxed{dU = T\,dS - p\,dV}$$

Now integrate $T\,dS = d(TS) - S\,dT$ and $p\,dV = d(pV) - V\,dp$ by parts

$$\boxed{dG = -S\,dT + V\,dp} \qquad \boxed{G \equiv U - TS + pV}$$

① The natural variables are T, p ; $G(T,p)$

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

So comparison gives

$$(\partial G/\partial T)_p = -S \qquad (\partial G/\partial p)_T = V$$

② The gibbs free energy is most useful for describing chemical reactions where temperature and pressure are fixed. Then one is interested in extracting work during the chemical process

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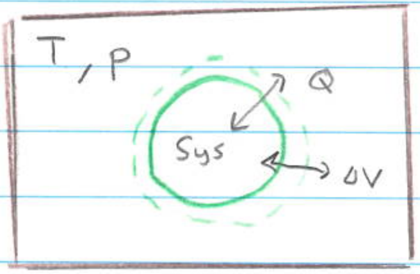
A generalization: Constant Temperature and Pressure

- Now we will have the Gibbs Free energy since the temperature and pressure are constant



We have a system exchanging heat with its environment at constant T and P

- In contrast with the previous case the system can change its volume. The total work done by the system is $\boxed{dW_{out} = p\,dV + dW^{other}_{out}}$. Prominent examples of "other" sorts of work are electrical and chemical work, e.g. photosynthesis.

$$dS_{sys} + dS_R \geq 0$$

$$dS_{sys} - \frac{dQ}{T} \geq 0$$

Now $\boxed{dQ = dU + p\,dV + dW^{other}_{out}}$. Plugging in and regrouping in terms of $G \equiv U - TS + pV$ we have

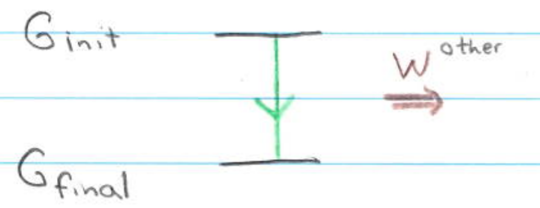
$$\boxed{-dG \geq dW^{other}_{out}} \qquad \boxed{G \equiv U - TS + pV}$$

- Similar statements apply, as in the free energy case Most importantly if no work is extracted in the process, $dW^{other}_{out} = 0$, and

$$\boxed{dG \leq 0}$$

i.e. this means that the Gibbs Free energy will evolve to a minimum.

- In general the drop in the Gibbs Free energy is the maximum electro-Chemical work that can be extracted from the process



$$G_{init} - G_{final} \geq W^{chem}_{out}$$