

## LECTURE 25. EQUILIBRIUM, FREE ENERGY AND TEMPERATURE

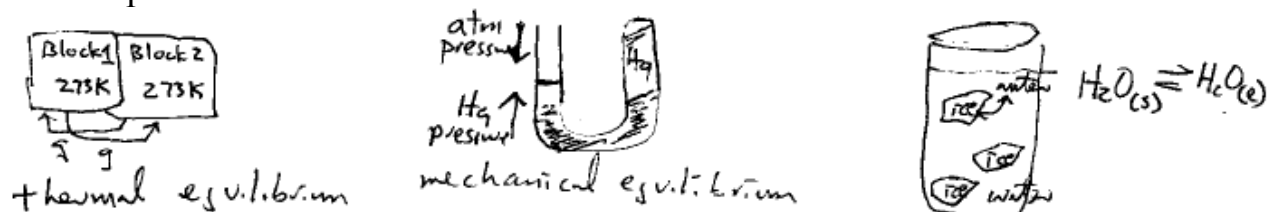
**Equilibrium:** We hinted at equilibrium while discussing thermodynamics (for example, noting that at a phase change, like melting or boiling, a system is at equilibrium)

But equilibrium is in fact so useful that we will spend 90% CH302 looking at.!

Equilibrium is defined for a system as having no tendency to change its current state. For a system at equilibrium, E, P, V, T, H, G, S retain the same value.

You can imagine equilibrium in many ways: thermal, mechanical, chemical.

For example:



**Dynamic Equilibrium:** Note that even though the overall state functions didn't change at equilibrium, on a molecular level there is plenty of action as molecules and energy transfer occur locally. For example, in a water-ice mixture, there are always ice molecules becoming liquid molecules and liquid molecules becoming ice molecules.

But the rate of the forward and reverse actions do not change. Hence from an external macroscopic vantage, nothing is changing.

### Definition of equilibrium:

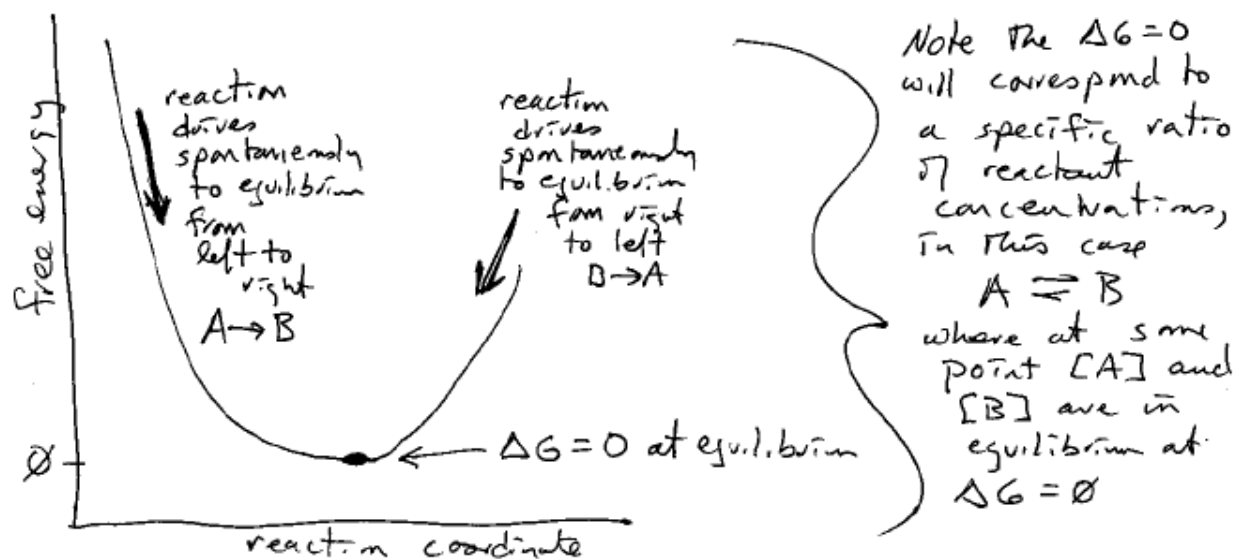
$$\Delta S_{\text{univ}} = 0 \text{ (or as we will see soon } \Delta G = 0)$$

This handy definition has already been exploited—recall that at a phase change (ice melting) we are at equilibrium so:

$$\Delta G = 0 = \Delta H - T\Delta S \quad \text{or} \quad T_{\text{boiling or freezing}} = \Delta H / \Delta S$$

↑  
Temperature of phase change

**Free Energy,  $\Delta G$ :** We have already learned that  $\Delta G$  is a measure of reaction spontaneity and have come to appreciate that it gives a sense of a reactions drive to completion. In the context of the new concept of equilibrium, we can construct a drawing that shows a reaction, from either direction, being driven by a release of energy to the surroundings, until  $\Delta G = 0$  at equilibrium.



So why you ask, do we bother with  $\Delta G$  if the measure of spontaneity from the second law is  $\Delta S_{\text{univ}} = 0$ ? The reason is that it is easier to take stock of **system** rather than **surrounding** parameters in determining spontaneity.

$$\Delta S_{\text{univ}} = \Delta S_{\text{surr}} - \Delta S_{\text{sys}}$$

↑

\*Yuck! Wouldn't it be better if this was a system function?

Well that is what  $\Delta G$  gives us. Spontaneity from system's state functions. Let's derive:

$$\Delta S_{\text{univ}} = \Delta S_{\text{surr}} - \Delta S_{\text{sys}}$$

$$\text{But } \Delta S_{\text{surr}} = -\Delta H_{\text{sys}} / T$$

So

$$\Delta S_{\text{univ}} = -\Delta H_{\text{sys}} / T - \Delta S_{\text{sys}}$$

Multiply through by  $-T$

$$-T \Delta S_{\text{univ}} = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$$

$$\text{Define } \Delta G = -T \Delta S_{\text{sys}}$$

$$\Delta G = \Delta H_{\text{sys}} - T \Delta S_{\text{sys}}$$

and we have our familiar Gibbs equation  
With  $\Delta H + \Delta S$  of system parameters!!!

## Temperature Dependence on Spontaneity

A bit of a review. Now that we have  $\Delta G = \Delta H - T\Delta S$  to determine spontaneity, we see that temperature controls the relative magnitude of  $\Delta H$  and  $\Delta S$ .

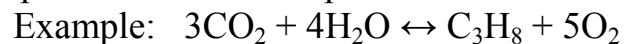
Consider four cases:

1.  $\Delta H$  is -,  $\Delta S$  is +: exothermic and system entropy increases. This means the reaction will happen because  $\Delta G$  is always negative at any temperature.



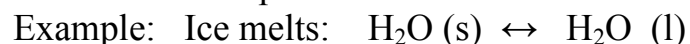
so  $\Delta S$  is positive because more molecules formed,  $\Delta H$  is negative because it is combustion

2.  $\Delta H$  is +,  $\Delta S$  is -: endothermic and system entropy decreases. This means the reaction will never happen because at any temperature  $\Delta G$  will be positive.



exactly the opposite of case 1 so it never happens

3.  $\Delta H$  is +,  $\Delta S$  is +: endothermic but entropy increases. This is a temperature dependent process and at high T, the negative  $T\Delta S$  dominates the positive  $\Delta H$  and the reaction occurs.



so  $\Delta S$  is positive because of the making of a liquid,  $\Delta H$  is positive because heat enters system and the reaction occurs at high temperature

4.  $\Delta H$  is -,  $\Delta S$  is -: exothermic but entropy decreases. This is temperature dependent. At low T the negative  $\Delta H$  dominates the positive  $-T\Delta S$  and the reaction occurs.

Example: Opposite of case 3, water freezes and the reaction occurs at low temperature

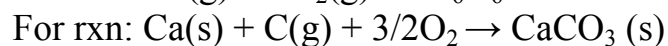
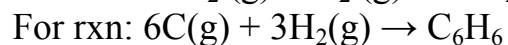
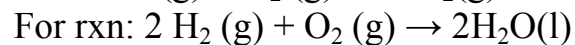
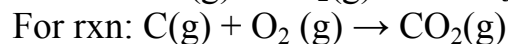
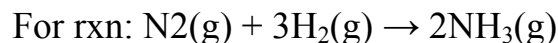
### $\Delta G^\circ_f$ : Gibbs free energy of formation: Compound stability

We have learned the convenience of formation reactions in calculating  $\Delta H_{\text{rxn}}$  from heats of formation,  $\Delta H^\circ_f$ , values compiled in tables. We then use these along with Hess's Law to calculate  $\Delta H_{\text{rxn}}$  for any reaction.

We can do the same with  $\Delta G^\circ_f$  values that are also tabulated.  $O_2$

Table of  $\Delta G^\circ_f$  (kJ/mol)

$NH_3$	-16
$CO_2$	-394
$H_2O$	-228
$C_6H_6$	+124
$CaCO_3$	-1128



We can use these values in any combination in the expression:

$$\Delta G^\circ_{\text{rxn}} = \sum \Delta G^\circ_f \text{ products} - \sum \Delta G^\circ_f \text{ reactants}$$

Similarly, we can calculate

$$\Delta H^\circ_{\text{rxn}} = \sum \Delta H^\circ_f \text{ products} - \sum \Delta H^\circ_f \text{ reactants}$$

And

$$\Delta S^\circ_{\text{rxn}} = \sum \Delta S^\circ_f \text{ products} - \sum \Delta S^\circ_f \text{ reactants}$$

And you will see that in combination:  $\Delta G^\circ_{\text{rxn}} = \Delta H^\circ_{\text{rxn}} - T\Delta S^\circ_{\text{rxn}}$

### Is a compound stable?

Wow, now we have a direct measure, from  $\Delta G^\circ_f$ , of whether a compound has the tendency to degrade into its elemental form.

$\Delta G^\circ_f \equiv -$  **means a compound is stable** and will not degrade. Examples from the table above are  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CaCO}_3$  all with  $-\Delta G^\circ_f$

$\Delta G^\circ_f \equiv +$  **means a compound is unstable** and will degrade. Benzene, with  $\Delta G^\circ_f = +124$  kJ/mole is unstable.

Labile means  $\Delta G^\circ_f$  is positive and compound degrades quickly

Nonlabile means  $\Delta G^\circ_f$  is positive and compound degrades slowly

So Benzene, which is unstable, can still hang around in bottles and cause cancer, so we describe it as non-labile. Hydrogen peroxide, which goes bad sitting on a kitchen counter, is unstable and labile.