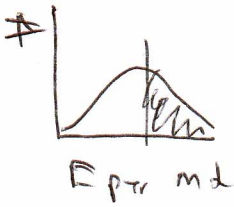
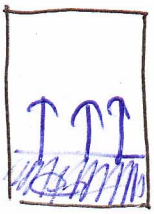
10/31/11

Vapor Pressure

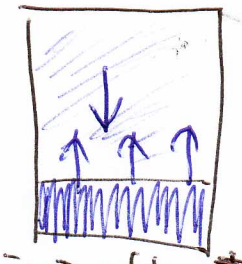


forward - evaporation
reverse - condensation

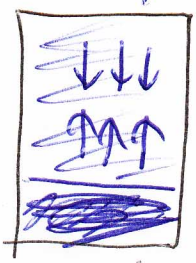
vapor ~~suddenly removed~~ suddenly added



T = 0
[P] = 0
$R_r = 0$; only forward



just after T = 0
$R_f > R_r$
some vapor now condensing



T = equilibrium
$R_f = R_r$
no more change in pressure

past equilibrium
[P] too great
$R_r > R_f$
condensation occurs

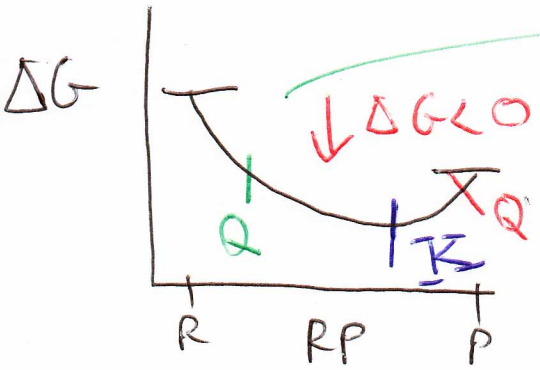
@ t = 0, liquid is introduced into a completely empty chamber (under vacuum)

Le Châtelier's principle -

When a system @ equilibrium is stressed (changed), the system will respond in a way that relieves that stress.

Q = reaction quotient

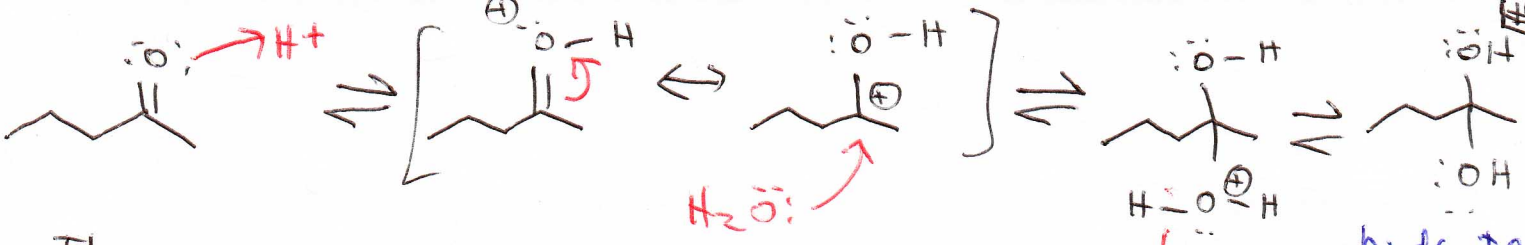
Q is mathematically identical to K, except K is only calculated at equilibrium concentrations, while Q can be calculated at any point in a rxn.



$Q = \frac{\text{products}}{\text{reactants}}$

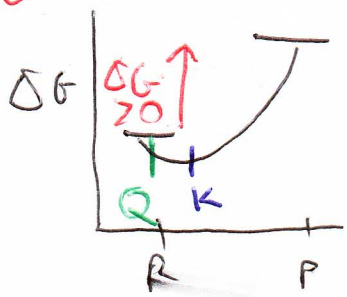
If Q<K, then not enough products have formed and/or there are too many reactants around.

If Q>K, then not enough reactants are present and/or too many products have formed.



This particular rxn is reversible and non-spontaneous ($\Delta G > 0$).

If products are suddenly removed when the rxn is @ equilibrium!



1) $Q < K$, since Q is $\frac{\text{products}}{\text{reactants}}$ and [products] just decreased

2) $R_f > R_r$, since products were removed (not reactants)

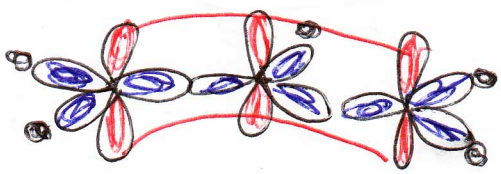
3) Potential E of the system is effectively increased.

∴ The rxn will move forward to make more products to reestablish equilibrium.

— If products are continuously removed as they form, the rxn can be forced to completion, even though it is non-spontaneous.

K is only affected by temperature, not [ ].

Delocalization



- Resonance structures only exist because the system used to write structures (LDS.) is unable to unambiguously represent bonds that cover more than two atoms.

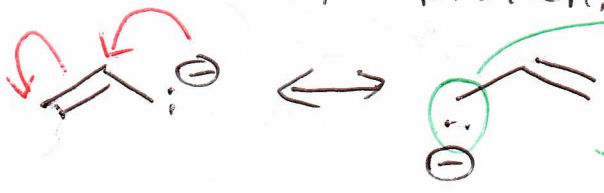
- No single resonance structure correctly reflects the true structure of a molecule.

#3

- The true structure of a molecule can be estimated by averaging all possible resonance structures together.

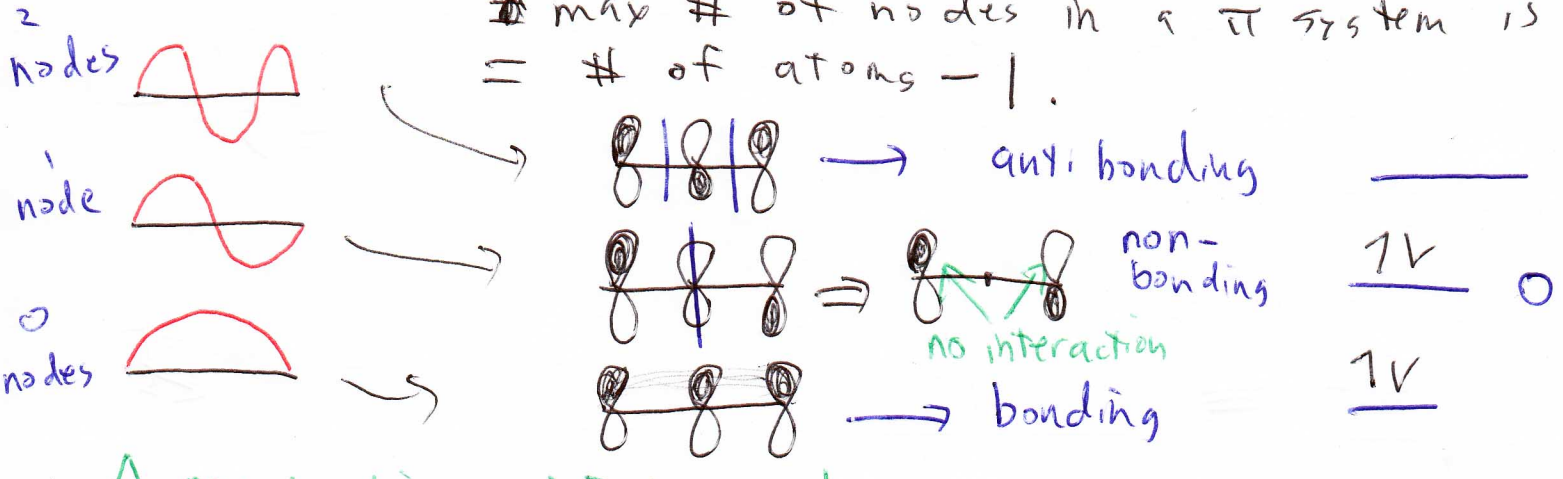
Rules for writing resonance structures

- Only lone pairs and π-bonds are able to move; single bonds can never be formed or broken.



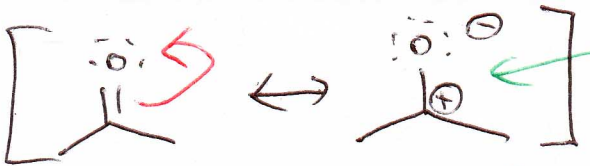
This carbon is actually sp^2 hybridized. It appears sp^3 in this resonance structure, but that is because resonance structures fail to show delocalized bonding.

max # of nodes in a π system is = # of atoms − 1.



A non-bonding orbital is the same in energy as the atoms if they had never undergone bonding.

- Better resonance structures generally have full octets (where possible), lack of charge separation, and charges that match electronegativity.



Unfavorable due to charge separation.

even worse since now O is positively charged.

#4