CHEM 206 section 01

LECTURE #16 Wed. March 5, 2008

LECTURE TOPICS:

TODAY'S CLASS: **start Ch.16 & 19.7**

NEXT CLASS: **Ch.16…**

Chapter 16: CHEMICAL EQUILIBRIA

- If reactions are reversible, won't the reverse reaction start competing with the forward reaction when products build up?
  YES… → link to kinetics
- How product-favoured or reactant-favoured is a reaction overall?
  → link to thermodynamics!

Chapter Outline

16.1 Nature of the equilibrium state
16.2 Reaction quotient (*Q*) & equilibrium constant (*K*)

19.7 ΔG^o, K & product-favorability

16.3 Determining an eq'm constant
16.4 Using eq'm constants in calculations
16.5 More about balanced equations & eq'm constants
16.6 Disturbing a chemical equilibrium
16.7 Applying the eq'm concept…

Chapter Goals

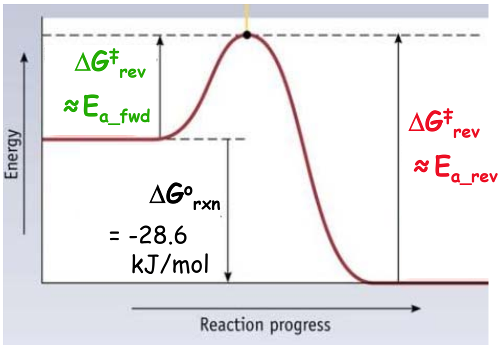
- Understand the nature and characteristics of chemical equilibrium
- Understand the significance of the equilibrium constant, K
- Understand how to use the eq'm constant in quantitative studies of chemical equilibrium

Chemical processes are reversible (16.1, 16.2)

Principle of "microscopic reversibility" :
all chemical processes <u>can</u> proceed in <u>both</u> directions

- HOWEVER: often EASIER in one direction (smaller E_a…)
- NET EFFECT: product-favoured *vs.* reactant-favoured?
  - ⇨ see ΔG_{rxn} …determines difference between fwd *vs* rev E_a

For rxn: $H_2O(g) + CO(g) \rightarrow CO_2(g) + H_2(g)$



$\Delta G^{o}_{rxn} < 0$ ⇨ product-favoured
(products more stable)

WHY we get mostly products:
Smaller E_a for fwd rxn
⇨ Larger rate constant k_{fwd}
⇨ fwd rxn inherently faster

BUT remember:
concentrations also play <u>important</u> role in rxn rate…

For a 1-step rxn: m Reactant $\rightleftharpoons$ n Product

Equilibrium = dynamic state where: $\text{Rate}_{fwd} = \text{Rate}_{rev}$

THUS: $k_{fwd}[\text{reactant}]^m = k_{rev}[\text{product}]^n$

Rearrange to group constants:

$$\frac{k_{fwd}}{k_{rev}} = \boxed{\frac{[\text{product}]^n}{[\text{reactant}]^m} = K_{eq}}$$

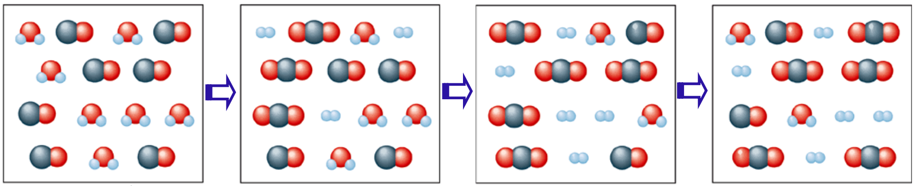
EQUILIBRIUM
CONSTANT

SHOW YOURSELF:
If fwd rxn's E_a is larger,
rxn is reactant-favoured (K<1)
& vice versa

Closed systems ultimately become equilibrated…

(as long as no material can enter or leave the system…)

$H_2O + CO \rightarrow CO_2 + H_2$ ΔG^o_{rxn}=-28.6 kJ (product-favoured)



Mix H_2O & CO

Rxn produces $CO_2 + H_2$…

$[H_2O]$ & $[CO]$ ↓

⇨ $rate_{fwd}$ ↓

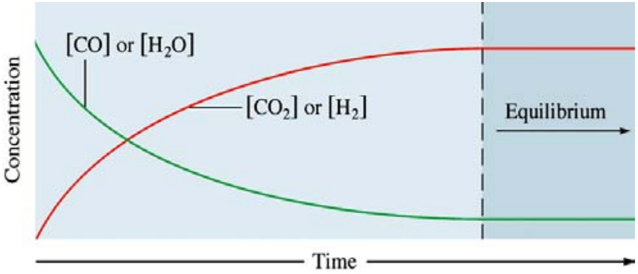
$[CO_2]$ & $[H_2]$ ↑

⇨ $rate_{rev}$ ↑

EQM reached:

$rate_{fwd} = rate_{rev}$

[ ]s stop changing



AT EQUILIBRIUM:

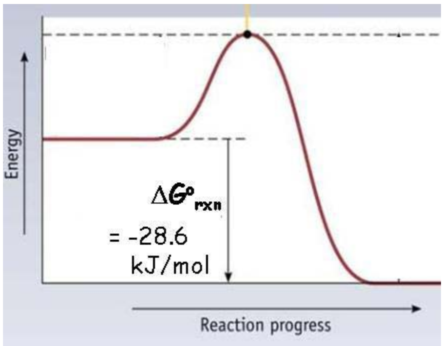
- no further change at macroscopic level
- BUT: **dynamic at molecular level…**

Z.Fig.13.2-3; Kotz Fig.16.3

19.7 ΔG^o, *K* and product-favourability: at equilibrium, the more stable state dominates

FIRST: SOME NECESSARY CLARIFICATIONS…

- ΔG^o = change in free energy if reactants (in std states) are converted completely to products (in std states)
- Describes relative stability of pure reactants *vs.* pure products
- **In reality: most reactions do not go to completion equilibrium is usually reached before then!**



ΔG^o < 0: product-favoured

- product state more stable
- magnitude tells us how much more… = theoretical driving force fwd
- some reactants may remain at eqm

ΔG^o > 0: reactant-favoured

- reactant state more stable
- magnitude tells us how much more…
- reaches eqm after only small quantity of product has formed

Before equilibrium: driving force at any moment depends on concentrations of species present…

Free energy difference between products & reactants
in **real mixture** at one moment = **driving force FOR <u>REAL</u> MIXTURE**

$$\Delta G = \Delta G^\circ_{rxn} + \underbrace{RT \ln Q}$$

(<u>don't</u> need to know derivation)

Corrects for substances NOT being in their standard states (*i.e.*, **not 1M / 1atm**)

Free energy of rxn
if reactants in **std states**
(1atm/1M/specific T)
are converted 100% to
products in std states

Where Q = "reaction quotient"

$$Q = \frac{[\text{products}]^n}{[\text{reactants}]^m}$$

Calculated using non-eqm concentrations (see 16.2)

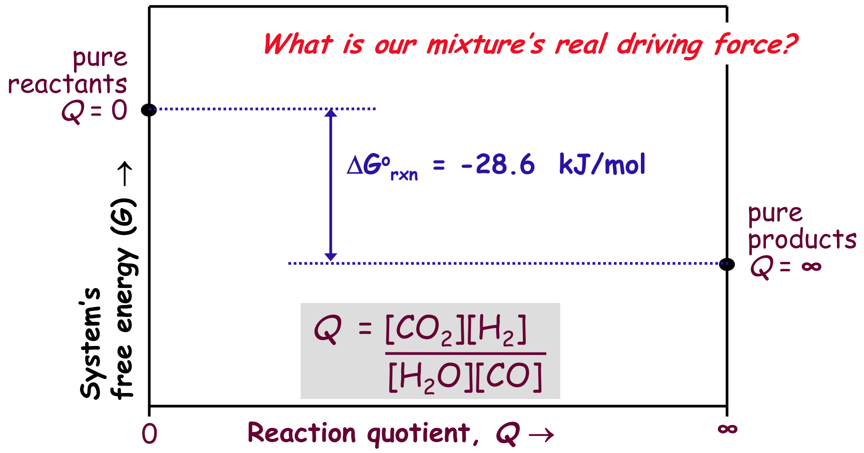
For rxn: m Reactants $\rightleftharpoons$ n Products

(7)

Thinking about driving force in a real mixture…

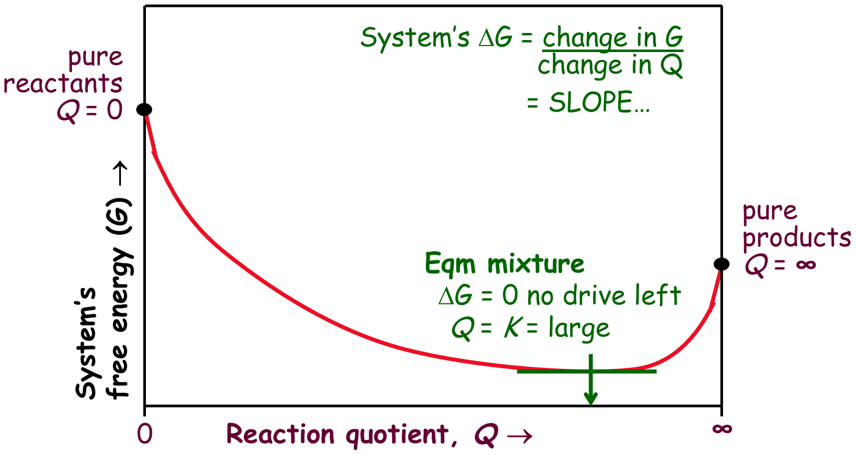
See Kotz Fig.19.13

For rxn: $H_2O(g) + CO(g) \rightarrow CO_2(g) + H_2(g)$



For rxn: $H_2O(g) + CO(g) \rightarrow CO_2(g) + H_2(g)$

In our real system: $\Delta G = \Delta G^\circ_{rxn} + RT\,\ln \dfrac{[CO_2][H_2]}{[H_2O][CO]}$

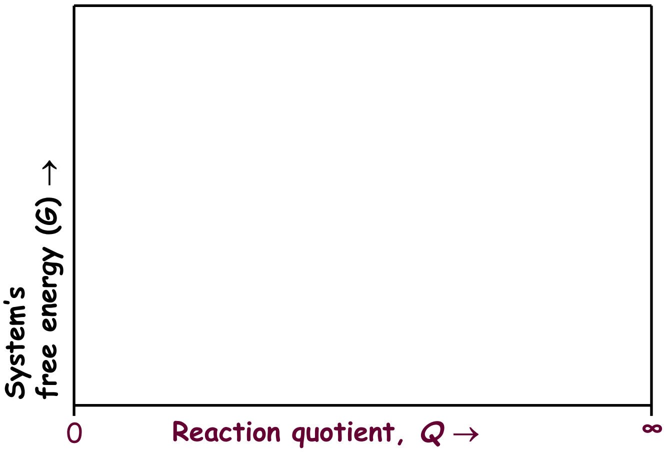


Q is constant at eqm (= *K*) for a given rxn at a given T & P.
Note: infinite combinations of actual [ ]'s can give this ratio…

For rxn: $2\ H_2O(\ell) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

$\Delta G^\circ = +78.2$ kJ/mol

Only occurs to a TINY extent.
Reverse rxn is enormously preferred.



Rxns proceed "downhill in energy" until reach equilibrium

i.e., until run out of net driving force (…$\text{rate}_{fwd} = \text{rate}_{rev}$)
…corresponds to mixture with $(G_{products} - G_{reactants}) = 0$

At eqm: $\Delta G°_{rxn} = -RT \ln K_{eq}$

where $K = Q_{eq} = \frac{[\text{products}]_{eqm}^{n}}{[\text{reactants}]_{eqm}^{m}}$

$\Delta G°$	K	*At eqm…*	*If mix reactants in std states…*
0	1	reactants & products	Already at equilibrium
< 0	> 1	products dominate	Driven to proceed forward
> 0	< 1	reactants dominate	Small amount of fwd rxn happens

Do not misinterpret the term "equilibrium constant":
- Eqm constants K change with temperature
- At eqm: [ ]s of products & reactants are related, not equal
- Eqm [ ]s are constant in a given eqm mixture
  - ⇨ K will be same no matter what the $[\ ]_o$s were
  - ⇨ BUT: infinite sets of actual $[\ ]_{eqm}$s can "satisfy" K

ASSIGNED READINGS:

BEFORE NEXT CLASS:

Read: Ch.16 section 16.1-16.2 & 19.7

+ WORK ON Problems from Ch.15