1/6 Chemical equilibrium (EQ)

reaction at equilibrium : $R \rightleftharpoons P$ [R] & [P] do not change.

at molecular level: rxn doesn't stop at equal rate.

at EQ : $K_c = \frac{[P]}{[R]}$ more [P] ⇒ more stable the pdt is.

under same conditions, rxn at EQ has same $\frac{[P]}{[R]}$ rate.

(thermodynamic relation: $\Delta G^\circ = -RT\ln K$ (later))

rxn at EQ : $aA + bB \rightleftharpoons cC + dD$ $K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$

{ a, b, c, d : stoichiometric coefficients of balanced equation.
{ [x] = concentration. (with units omitted)

(activity: more precise way to describe K_c. (though most books makes it equal to concentration).
$a_R = \gamma_R [R]$ activity : no units.)

K_c doesn't have unit.

eg: Calculate K_c for N_2 mixed w/ H_2 at 500°C to produce ammonia

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

at EQ : $[N_2] = 0.305\ M$, $[H_2] = 0.324\ M$, $[NH_3] = 0.796\ M$

A: $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \boxed{61.0}$

if in reverse rxn : $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$. keep [x] the same.

get : $K_{c_{new}} = \frac{1}{K_c} = \frac{1}{61.0}$

1/8

- All R&P in same phase : homogeneous EQ
- One or more R or P in different phase : heterogeneous EQ
- Molar (concentration) conc. of a Pure substance (solid or liquid) doesn't change in a rxn ⇒ Pure substances are not included in K expression.

  eg: $Ca(OH)_2\,(s) \rightleftharpoons Ca^{2+}(aq) + 2\,OH^-(aq)$ $K_c = [Ca^{2+}][OH^-]^2$

  Do not put solvents into the rxn eq.

  H_2O omitted: change in solvent conc. is insignificant.

- For a gas, use its partial pressure (p) and EQ constant is denoted by K_p.

  e.g.: $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $K_p = P_{CO_2}$

  $P_{total} = \sum P_{partial}$

  $K_p = \frac{P_P}{P_R}$

- Convert between partial pressure & concentration for a gas:

  ideal gas law: $PV = nRT$ (approx.) ⇒ $P = \frac{nRT}{V} = conc. \times RT$

  P: pressure (Pa.)
  V: volume (L)
  n: # moles. (mol)
  R: 8.314 ($\frac{J}{mol \cdot K}$) $J = kg \times m^2/s^2$
  T: temperature (K)

EQ constant, K, tells us

- If K is small ($K < 10^{-3}$) More reactants at EQ.

  $R \rightleftharpoons P$ (EQ sits to the left)

  $K = 1$ is rare

  K is large ($K > 10^{3}$) More pdts at EQ

  $R \rightleftharpoons P$ (EQ sits to the right)

  intermediate values of K ($10^{-3} < K < 10^{3}$)

  neither R nor P strongly favored

Use K to calculate the partial pressure (conc.) of a species at EQ

eg: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ at 298 K

at EQ $K_p = 25$, $P_{PCl_5} = 0.0021$ atm, $P_{Cl_2} = 0.48$ atm.

What is P_{PCl_3} at EQ.

A: $K_p = \frac{P_{PCl_3} \cdot P_{Cl_2}}{P_{PCl_5}}$

$\Rightarrow P_{PCl_3} = \frac{K_p \cdot P_{PCl_5}}{P_{Cl_2}}$

$= \frac{25 \times 0.0021}{0.48} = \boxed{0.11 \text{ atm}}$

Determine the direction of a reaction will proceed.

$$K_c = \frac{[P_{EQ}]}{[R_{EQ}]}$$

$$Q = \frac{[P \text{ measured}]}{[R \text{ measured}]}$$ at a random time during the rxn and compare it w/ K

(Q → rxn quotient)

If:
- $Q < K$ at some time during the rxn, then measured $[R] > [P]$
  ⇒ forward rxn is favored.
- $Q = K$ at EQ.
- $Q > K$ at some time during the rxn, then $[P] > [R]$
  ⇒ reverse rxn is favored.

eg: nitrogen dioxide is produced by the rxn

$$N_2O_4 (g) \rightleftharpoons 2 NO_2 (g) \qquad K = 1.7 \times 10^3$$

when $P_{NO_2} = 0.5$ atm and $P_{N_2O_4} = 0.5$ atm is the system at EQ

If not, which direction?

A: $Q = \frac{P_{NO_2}^2}{P_{N_2O_4}} = \frac{0.5^2}{0.5} = 0.5$

$Q < K_p$ ⇒ not at EQ, proceeds towards pdts.

1/10 e.g.: 1.50mol PCl_5 is placed in a 500 mL reaction vessel and decomposes at 250°C to form PCl_3 & Cl_2. $K_c = 1.80$. All 3 compounds are gases at 250°C

Composition of the EQ mixture? $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

A: Assume PCl_5 decreased by x mol/L

ICE table

	$PCl_5(g)$	$\rightleftharpoons PCl_3(g)$	$+ Cl_2(g)$
I	$\frac{1.50mol}{0.5L} = 3.00M$	0	0
C	$-x$	$+x$	$+x$
E	$3-x$	x	x

$K_c = \frac{x^2}{3.00-x} = 1.80$

$x = 1.59$

$[PCl_5]_f = 3.00 - 1.59 = 1.41\ M$

$[PCl_3]_f = [Cl_2]_f = 1.59\ M.$

- Response of EQ to change.
  - Change in conc. (K does not change)

  Chemical rxn at EQ represents a fixed P/R ratio.

  What happens when more reactant is added? rxn goes toward right

  $R \rightleftharpoons P$ K means at EQ,

  $K = \frac{[P]}{[R]}$ wait for the system to reach EQ again (K is the same)

  What happens when more pdt is added? rxn goes toward left

What does this tell us about chemical rxns?

Chemical rxns adjust so as to minimize the effect of changes

Le Chatelier's principle

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

What happens if we
- increase N_2 ⇒ left
- increase NH_3 ⇒ right
- decrease H_2 ⇒ right.

W/o adding more reactants, how would you increase yield of NH_3?

Remove NH_3

Le Chatelier's principle also applies to changing physical parameters (P & T)

- Change in pressure (K does not change)

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ How does a rxn respond to minimize the effect of increasing pressure (By decreasing volume)?

n constant $c = \frac{n}{V}$ conc. increases.

If initial conc. at EQ is 0.1 0.1 0.1 M

Then $K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.1)^2}{0.1 \times (0.1)^3} = 100.$

Volume is halfed, all conc. are doubled

⇓

P is doubled.

∴ new conc. ⇒ 0.2, 0.2, 0.2 M

Then $Q = \frac{(0.2)^2}{0.2 \times (0.2)^3} = 25$

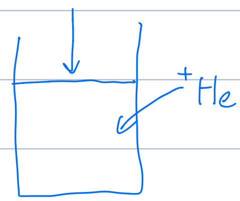
∴ $Q < K$

∴ rxn shifts right.

(Quick way:
V decreases & more moles of gas on left, then rxn shifts right.)

The system is NOT respond to change in pressure
is respond to change in conc.

e.g.



pressure doubles, V same, conc. same.
rxn does NOT shift