Ch. 15.7 LeChatelier's principle

- used to describe how a Rx @ equilibrium responds to a disturbance to the Rx
- like homeostasis ≈ "do the opposite"

review: Q, reaction quotient

$$aA + bB \rightleftharpoons cC + dD$$

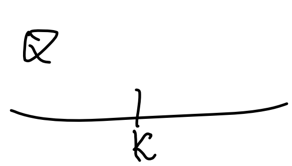
$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

[ ] are not @ equilibrium

notes: if $Q = K$, then the Rx is @ equilibrium

- if $Q \neq K$, then the Rx is not @ equilibrium
  - $Q > K$ — to reestablish equilibrium: $\downarrow Q \rightarrow \downarrow$ [products], $\uparrow$ [reactants]

- if $Q < K$ — to reestablish equilibrium: $\uparrow Q \rightarrow \uparrow$ [products], $\downarrow$ [reactants]



recall/reminder: K is a function of T
so if constant T, then the value of
K is a constant

problems: $N_2 + 3H_2 \rightleftharpoons 2NH_3$

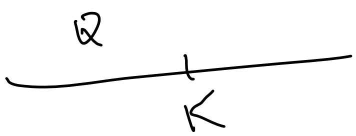
$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(\frac{n_{NH_3}}{V}\right)^2}{\left(\frac{n_{N_2}}{V}\right)\left(\frac{n_{H_2}}{V}\right)^3}$$

$$\boxed{Q = \frac{n^2_{NH_3} V^2}{n_{N_2} n^3_{H_2}}}$$

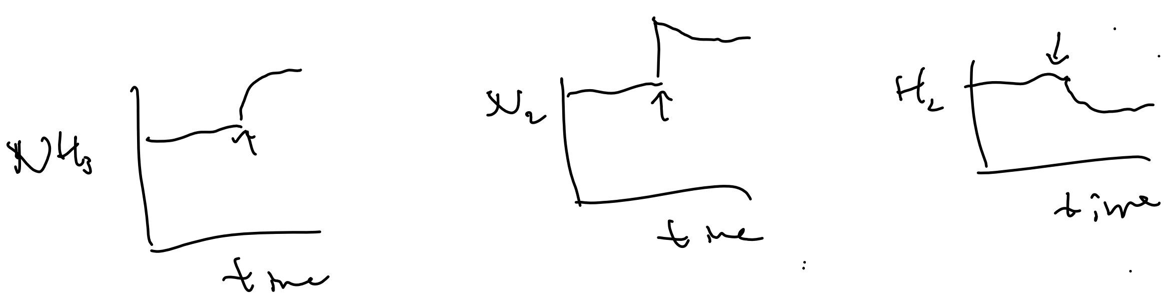
@ constant T

(1) add N_2 @ constant T & V; effect n_{NH_3}?
n_{H_2}?

add $N_2 \rightarrow \uparrow n_{N_2} \rightarrow \downarrow Q \rightarrow$ to reestablish equilibrium $\rightarrow \uparrow Q$



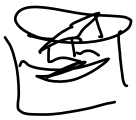
$\uparrow r_b \leftarrow \uparrow NH_3 \leftarrow \uparrow Q$
$\downarrow$
$\downarrow n_{H_2}$



(2) add N_2 @ constant T & P; effect on,
n_{NH_3}?
n_{N_2}?

add N_2 → ↑ n_{N_2} → ↓ Q

↳ ↑ n_{total} → ↑ P_{total} → ↑ V → ↑ Q



← movable piston

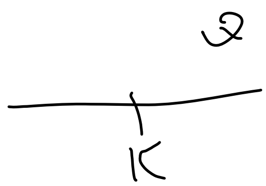
effect on Q is ambiguous; thus unable to describe the Rx's response

③ add He @ constant V & P; effect on n_{NH_3}? n_{N_2}?

∃ no change in Q → Rx still @ equilibrium → no change in n_{NH_3} or n

④ add He @ constant T & P; effect on n_{NH_3}? n_{N_2}?

add He → ↑ n_{total} → ↑ P_{total} → ↑ V → ↑ Q



↓ to reestablish equilibrium → ↓ Q

↑ n_{N_2} ← ↑ n_{H_2} ← ↓ n_{NH_3}

⑤ remove H_2 @ constant T & V; effect on n_{NH_3}? n_{N_2}?

remove H_2 → ↓ n_{H_2} → . . . ↓ n_{NH_3}

↑ n_{N_2}

⑥ ↓ V @ constant T; effect on n_{NH_3}? n_{N_2}?

↓ V → ↓ Q → --- ↑ n_{NH_3}

↓ n_{N_2}

② $\uparrow T$ @ constant V; effect on n_{NH_3}?

n_{N_2}?

need to evaluate ΔH

<u>method 1</u> "simple"

recall: $\Delta H_{Rx} = \sum a\, \Delta H_f(P) - \sum b\, \Delta H_f(R)$

$\Delta H_{Rx} < 0$

generate q; exothermic Rx

$N_2 + H_2 \rightleftharpoons NH_3 + q$

$\uparrow T \rightarrow$ "like" $\downarrow T$ = consume $q \rightarrow \uparrow r_b$

$\downarrow$

$\downarrow n_{NH_3}$

$\uparrow n_{N_2}$

<u>method 2</u>: "complicated"

<u>background</u>: ch 19.7

$\Delta G = \Delta G^\circ + RT\ln Q$

$\Delta G^\circ = \sum a\, \Delta G(P) - \sum b\, \Delta G(R)$

@ equilibrium

$\Delta G = \Delta G^\circ + RT\ln K = 0$

$$\boxed{\Delta G^\circ = -RT\ln K}$$

relates thermodynamics to equilibrium

review

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad [1]$$

$$\Delta G^\circ = -RT\ln K \quad [2]$$

subst [2] into [1] (or use the transitive property)

$$-RT\ln K = \Delta H^\circ - T\Delta S^\circ$$

$$\boxed{\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}}$$

aside/note:

graph of $\ln K$ vs $\frac{1}{T}$ can be used to estimate ΔS° & ΔH°

note: $\exists$ a relationship between K & T which depends if $\Delta H^\circ > 0$ or $\Delta H^\circ < 0$

notes:

- if $\Delta H < 0$

ignore "$\frac{\Delta S^\circ}{R}$" term b/c it's not affected by T

$$\ln K = \sim + \frac{\Delta H^\circ}{RT}$$

$$\uparrow T \rightarrow \downarrow \frac{\Delta H^\circ}{RT} \rightarrow \downarrow \ln K \rightarrow \downarrow K$$

as $K = \frac{[\text{products}]}{[\text{reactants}]}$

$\downarrow$ [products]
$\uparrow$ [reactants]

• if $\Delta H > 0$

$$\ln K = \sim\sim - \frac{\Delta H}{RT}$$

$\uparrow T \rightarrow \downarrow \frac{\Delta H}{RT} \rightarrow \uparrow \ln K \rightarrow \uparrow K \rightarrow$ $\uparrow$ [products] $\downarrow$ [reactants]

subtracting a smaller neg #

---

ask in return: $\Delta H < 0$; effect $\uparrow T$ on n_{NH_3}?

... $\downarrow n_{NH_3}$