What is equilibrium?

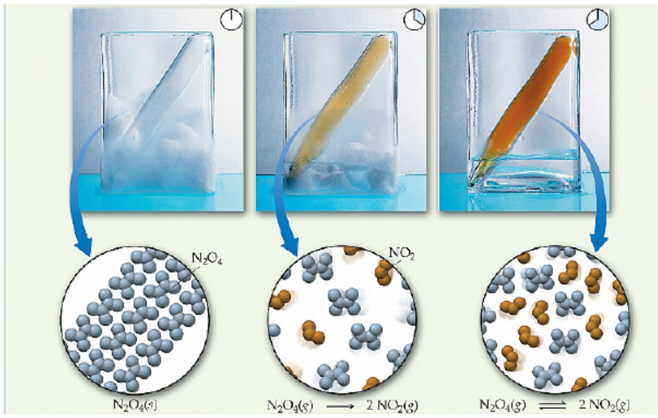
Equilibrium: *to be in a state of balance*

Static Equilibrium: *an object subject to equal & opposite forces is at rest (physics)*

Dynamic Equilibrium: *opposing processes occur simultaneously & at the same rate*

- *So change is happening, but the situation seems static*

Chemical Equilibrium: *reversible chemical reactions occur in the forward & backward directions simultaneously & at identical rates*



In a closed system, the [reactants & products] appear static.

Actually, both are constantly being made & broken down, but their concentrations do not change so the Situation appears to be static.

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Equilibrium reactions are reversible.

When a sealed test tube of dinitrogen tetroxide is placed into a beaker of warm water a reversible reaction starts. Because the tube is sealed (a closed system) it eventually reaches equilibrium.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

colorless — *brown*

We can write rate equations for each reaction:

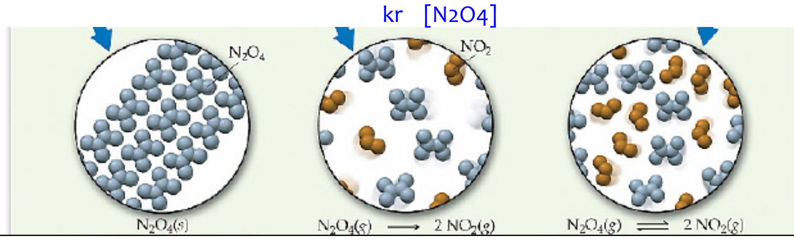
Forward rxn: Rate f $= k_f[N_2O_4]$

Reverse rxn: Rate r $= k_r[NO_2]^2$

At equilibrium: Rate f = Rate r $\quad k_f[N_2O_4] = k_r[NO_2]^2$

Rearrange to: $K_c = \frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]}$

Keq is a constant for each & every reaction



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CHE1031 Lecture 11: Chemical equilibrium

Lecture 11 topics	**Brown chapter 1**
1. Concept of equilibrium • Equilibrium reactions are reversible	15.1
2. The equilibrium constant **• Law of mass action** **• Equilibrium constant expressions**	**15.2**
3. Working with equilibrium expressions • What does Kc tell us? • Kc & direction of reaction	15.3
4. Le Chatelier's Principle • Application to Haber reaction • Changes of concentration • Changes in volume & pressure • Changes in temperature	15.7
5. Catalysts & equilibrium	

Equilibrium constant (Keq or Kc)

Law of mass action

Equilibrium constant expression

Using equilibrium expressions

Use the data presented below to determine the Kc for this reaction:

$$N_2O_4(g) \rightleftharpoons 2NO_2$$

$$Kc = \frac{[NO_2]^2}{[N_2O_4]} = \frac{[0.0172]^2}{[0.00140]} = 0.211$$

Note: **any** corresponding equilibrium concentrations can be used to calculate Kc.

TABLE 15.1 ■ Initial and Equilibrium Concentrations of N_2O_4 and NO_2 in the Gas Phase at 100 °C

Experiment	Initial $[N_2O_4]$ (*M*)	Initial $[NO_2]$ (*M*)	Equilibrium $[N_2O_4]$ (*M*)	Equilibrium $[NO_2]$ (*M*)	K_c
1	0.0	0.0200	0.00140	0.0172	0.211
2	0.0	0.0300	0.00280	0.0243	0.211
3	0.0	0.0400	0.00452	0.0310	0.213
4	0.0200	0.0	0.00452	0.0310	0.213

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Direction of reaction?

If you've calculated Kc for the forward reaction, the Kc for the reverse reaction is simply the inverse: **1/Kc**

$N_2O_4 \rightleftharpoons 2NO_2$ $K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212$ @ 100°C

$2NO_2 \rightleftharpoons N_2O_4$ $K_c = [N_2O_4] = \frac{1}{\quad} = 4.27$ @ 100°C

The equilibrium constant for the reaction shown below is, $K_c = 1\text{x}10^{-30}$ @ 25C.

$N_2 + O_2 \rightleftharpoons 2NO$

So, write the equilibrium expression, and calculate Kc for this reaction:

$2NO \rightleftharpoons N_2 + O_2$

$$K_c = \frac{[N_2][O_2]}{[NO]^2} = \frac{1}{K_c} = \frac{1}{1\text{x}10^{-30}} = 1\text{x}10^{30}$$

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CHE1031 Lecture 11: Chemical equilibrium

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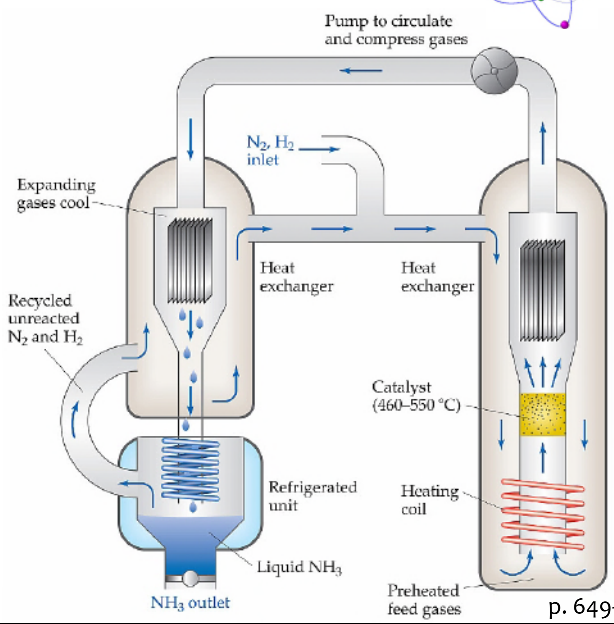
Applying Le Châtelier's to the Haber rxn

$N_2 + 3H_2 \rightleftarrows 2NH_3$

How is ***Le Chatelier's Principle*** employed here to increase production of NH3?

- NH3 is cooled, condensed and collected.
- When it's removed from the system it's loss shifts equilibrium to the right…
- … causing more NH3 product to be made.



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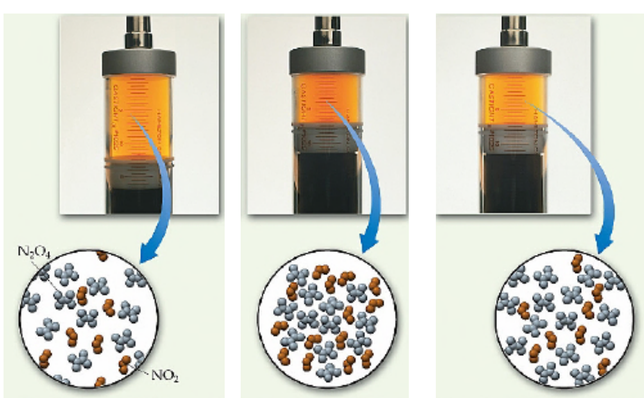
Changes in volume & pressure

Changes in volume tend to cause changes in pressure that "disturb" the system.

Reducing volume increases pressure and that shifts equilibrium in whichever direction reduces moles of gas….*and vice versa.*

$N_2O_4 \rightleftarrows 2NO_2$



1. Initial equilibrium
2. Plunger decreases volume & increases pressure & concentration, particularly of NO2.
3. Equilibrium has *shifted left* in ***order to decrease the moles*** of gas in cylinder.

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Another Le Châtelier's example

Consider this equilibrium reaction:

$$N_2O_4 \rightleftharpoons 2NO_2 \qquad \Delta H = +58 \text{ kJ}$$

In which direction does the reaction shift when:
a) N_2O_4 is added
b) NO_2 is removed
c) Pressure Is increased by addition of N_2
d) Volume is increased
e) Temperature is decreased

a) Shifts right towards product, driven by added reactant.
b) Shifts right towards the now depleted product
c) Shifts left since there are only half as many moles of reactant as product
d) Shifts right since the larger volume can accommodate more moles
e) Shifts left since the reaction is endothermic and requires heat as reactant. Reducing the heat is like reducing [reactant].

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Chapter 15: Terms to Know

- Static equilibrium
- Dynamic equilibrium
- Chemical equilibrium
- Forward & reverse reactions
- Haber reaction
- Law of Mass Reaction
- Equilibrium expression
- Le Châtelier's Principle
- "disturbance"