

Week 8

# Chemical Equilibrium



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# for administrative matters



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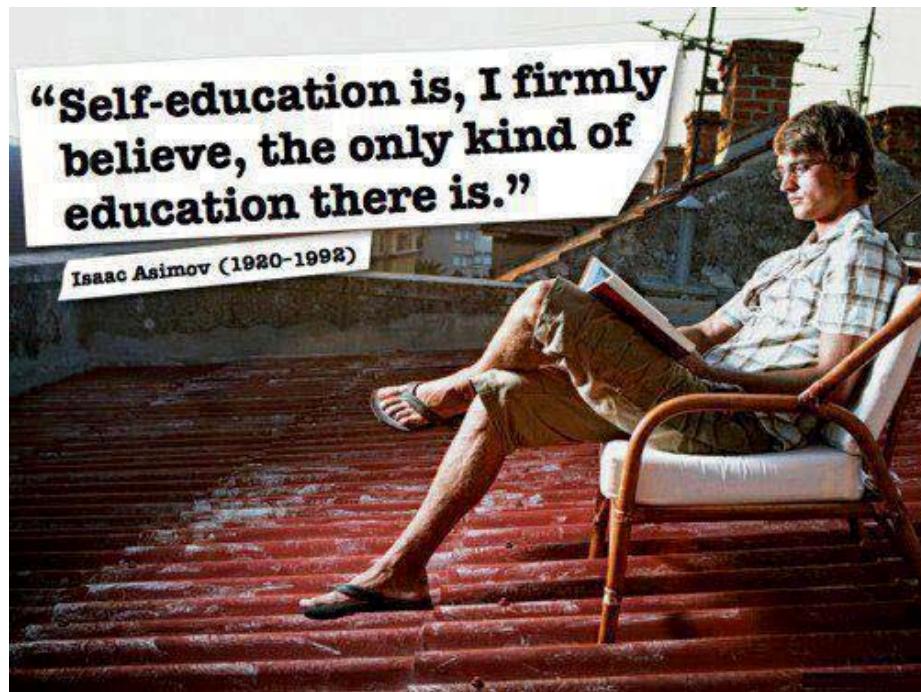
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## How to study & learn for this course ?



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*Some of these lecture topics are difficult:*



**you will have to put some effort in!!**

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***These lectures... yep, there's work for **you*****

### LECTURES

The online lecture notes are deliberately incomplete.



All material will be covered in lectures.

So either: • Attend all lectures and complete the notes

as we go (by far the easiest & best)

or              • Listen to the lecture recordings and complete the notes (very much harder)

### WORKSHEETS (for you to check your progress = **feedback**)

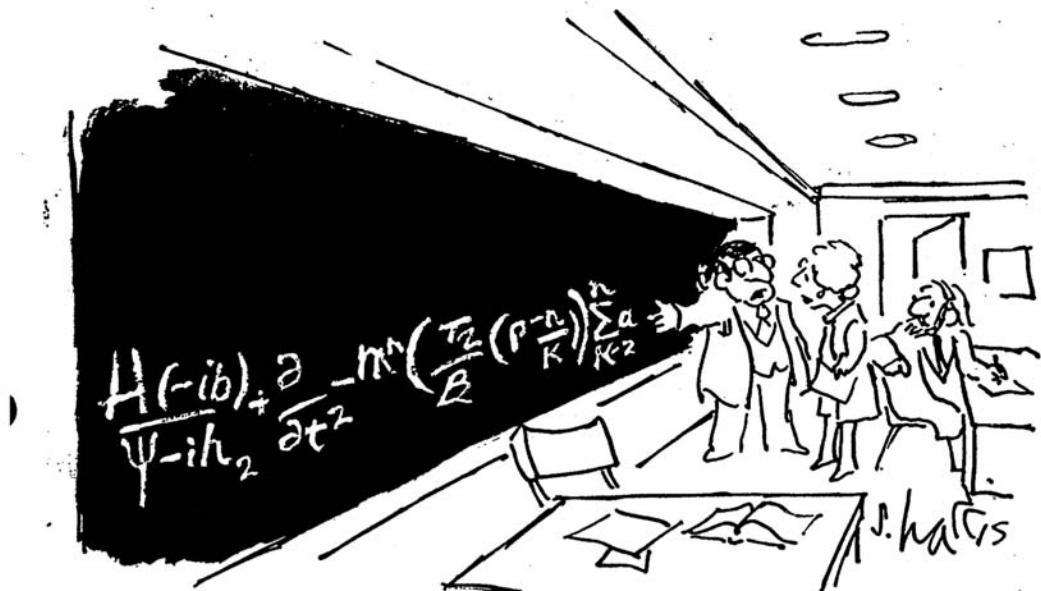
Each worksheet will only be handed out in the two lectures preceding the class in which it is gone over.

For you to get maximum benefit, attempt these (past exam) questions prior to them being worked through in class.

The worksheet questions and answers will not be posted online.

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## We'll keep it simple ...



"Yeh! this is the simplified version for CHEM1011"

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What  
defines...  
“Equilibrium”?

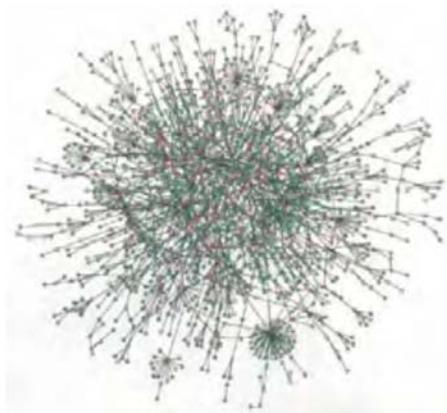


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# Life is far-from-equilibrium

Some far-from-equilibrium systems

Interactions between...



yeast proteins



internet nodes

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## Far-from-equilibrium systems



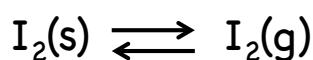
... are characterised by catastrophic fluctuations or failures, often irreversible !!



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# Chemical systems at equilibrium

... are simpler



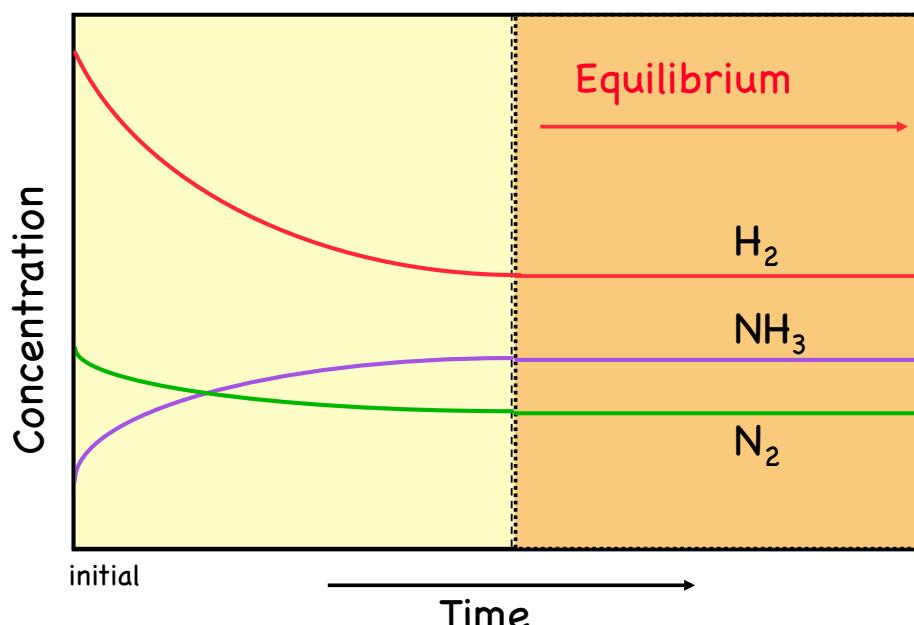
- what characterises them ?
- how do they react to (small) changes ?
- how to use equilibrium data

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## Equilibrium

[Blackman, 9.1]

- Not all reactions go to completion:

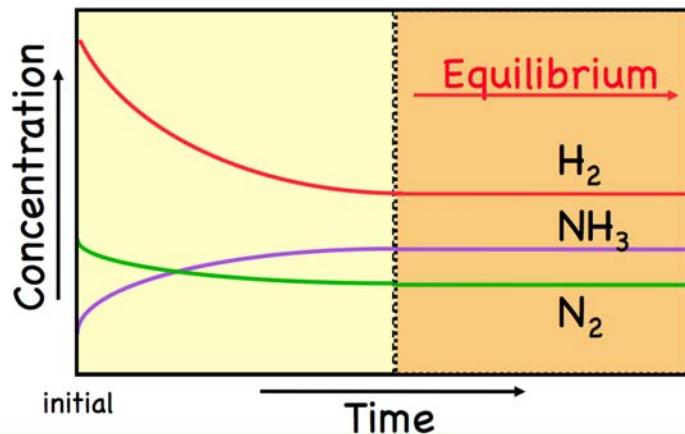
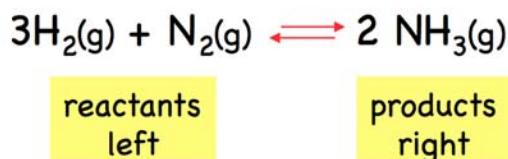


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# Equilibrium

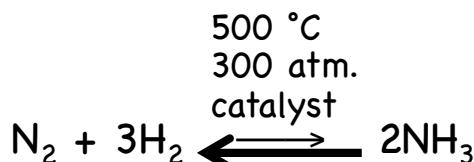
- As a reaction that doesn't go to completion proceeds:  
concentrations of reactants decrease  
⇒ rate of forward reaction decreases  
concentrations of products increase  
⇒ rate of reverse reaction increases)
- Equilibrium is reached when  
**rate** (forward reaction) = **rate** (reverse reaction)

- Equilibrium is **dynamic**  
(i.e. the reaction  
*never stops, but*  
goes nowhere!)



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## Ammonia and Fritz Haber



The Haber process  
(~2% world economy)

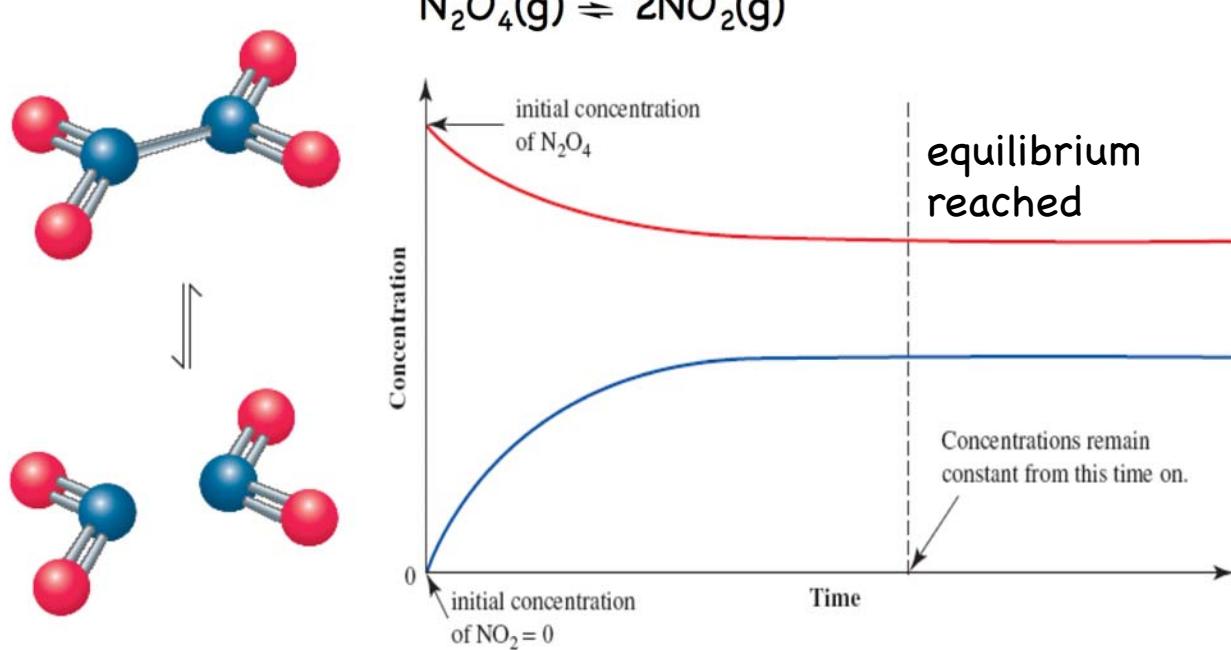


Fritz Haber (1868-1934)

- invented the Haber Process  
source of nitrate for Germany's munitions manufacture in WWI;  
1918 Nobel Prize for Chemistry
- personally directed the first use of chlorine as a war gas in WWI;  
on his return from the front, his wife killed herself using  
his army service revolver
- Jewish... invented Zyklon B; forced into exile from Germany in 1933

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# Equilibrium



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## Equilibrium constant

[Blackman 9.2]

When equilibrium is established for:



$$K_c = \frac{[\text{Y}/c^\ominus]^y [\text{Z}/c^\ominus]^z}{[\text{A}/c^\ominus]^a [\text{B}/c^\ominus]^b}$$

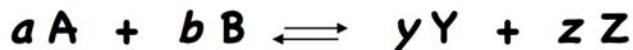
is the equilibrium constant

- **dependent on temperature;** so must always specify the temperature ( $T$ ) when  $K_c$  is reported
- **unitless:**  $c^\ominus$  is the *standard state concentration* of the substance (= 1.0 mol L<sup>-1</sup> for solute species in solution)
- **pure solids & liquids are omitted** from the equilibrium expression (the concentration of a pure solid or liquid is a constant, and does not affect the position of a heterogeneous equilibrium or the equilibrium constant; see later for why)

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## Equilibrium constant

For the general equilibrium:



You can use...

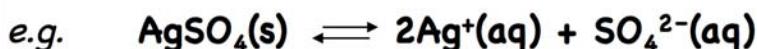
$$K = \frac{[Y]^y [Z]^z}{[A]^a [B]^b} \quad \text{for the equilibrium constant}$$

**provided** you recognise that you are...

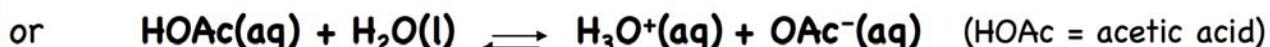
implicitly dividing by each concentration by  $c^\ominus$  (mol L<sup>-1</sup>),  
so **K is unitless**.

## $K_c$ for reactions involving Pure Substances

The concentrations of pure solids and pure liquids are ‘omitted’ from the equilibrium constant expression:



$K = [\text{Ag}^+]^2[\text{SO}_4^{2-}]$  so where does the concentration of solid  $\text{Ag}_2\text{SO}_4$  go?



$K = \frac{[\text{H}_3\text{O}^+][\text{OAc}^-]}{[\text{HOAc}]}$  so what is the concentration of liquid water and where does go?

- Ans: Need to think about: what is the concentration of the pure solid or pure liquid (standard state) and (how) does it change during a reaction

For example: what is the concentration of water? **Calculate it !**

# Equilibrium constant

General equilibrium:



$$K = \frac{[Y/c^0]^y [Z/c^0]^z}{[A/c^0]^a [B/c^0]^b}$$
 is the **equilibrium constant**

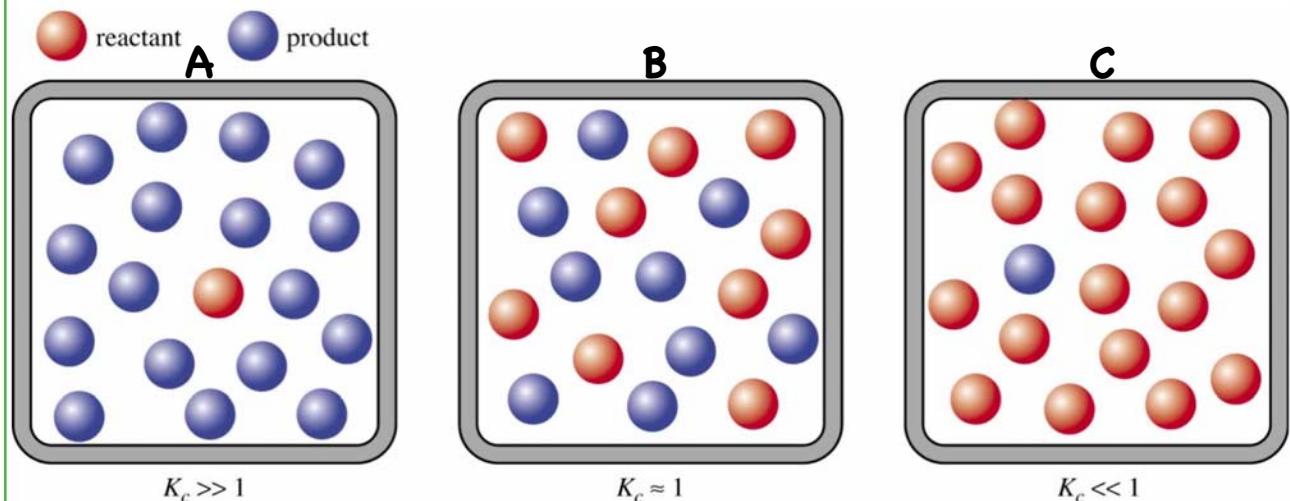
**Extent of reaction:** for a particular equilibrium reaction, if

$K \gg 1$  (large) ... equilibrium lies towards **products**

$K \sim 1$  ... similar concentrations of  
**reactants and products**

$K \ll 1$  (small) ... equilibrium lies towards **reactants**

## Extent of reaction from K



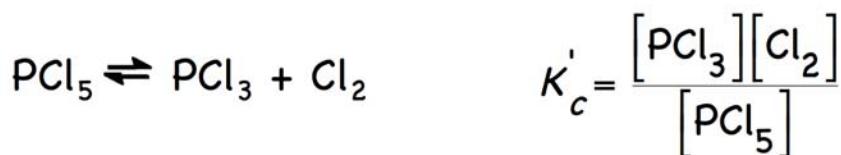
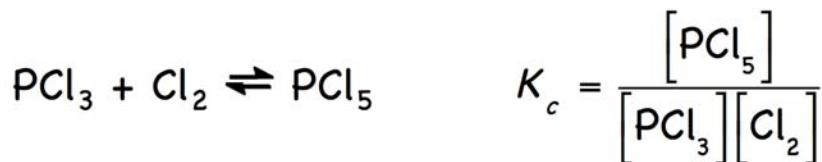
C  $K =$

B  $K =$

A  $K =$

## Manipulating equilibrium constant expressions

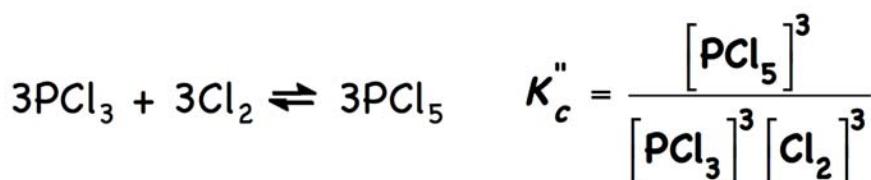
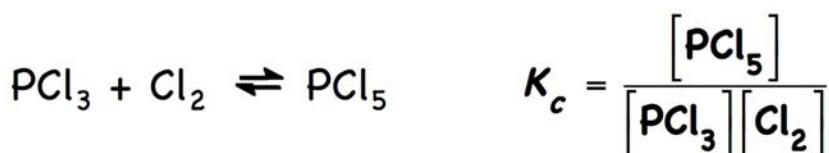
When the direction of an equation is reversed, the new equilibrium constant is the reciprocal of the original



$$K'_c = \frac{1}{K_c}$$

## Manipulating equilibrium constant expressions

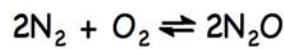
When the coefficients in an equation are multiplied by a factor, the equilibrium constant is raised to a power equal to that factor.



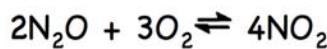
$$K''_c = K_c^3$$

## Manipulating equilibrium constant expressions. 3

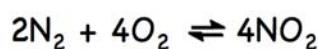
When chemical equilibria are added, their equilibrium constants are multiplied.



$$K_{c1} = \frac{[\text{N}_2\text{O}]^2}{[\text{N}_2]^2[\text{O}_2]}$$



$$K_{c2} = \frac{[\text{NO}_2]^4}{[\text{N}_2\text{O}]^2[\text{O}_2]^3}$$



$$K_{c3} = \frac{[\text{NO}_2]^4}{[\text{N}_2]^2[\text{O}_2]^4}$$

$$\frac{[\text{N}_2\text{O}]^2}{[\text{N}_2]^2[\text{O}_2]} \times \frac{[\text{NO}_2]^4}{[\text{N}_2\text{O}]^2[\text{O}_2]^3} = \frac{[\text{NO}_2]^4}{[\text{N}_2]^2[\text{O}_2]^4}$$

$$K_{c1} \times K_{c2} = K_{c3}$$

## Calculating values of $K$

### Example Question

Q. The Haber process (for industrial production of ammonia) produces the following equilibrium concentrations at 127 °C:

$$[\text{NH}_3] = 3.1 \times 10^{-2} \text{ mol/L}$$

$$[\text{N}_2] = 8.5 \times 10^{-1} \text{ mol/L}$$

$$[\text{H}_2] = 3.1 \times 10^{-3} \text{ mol/L}$$

(a) Calculate  $K$  for:  $3\text{H}_2 + \text{N}_2 \rightleftharpoons 2\text{NH}_3$

A. 
$$K = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3 [\text{N}_2]} =$$

Reaction, equil<sup>m</sup> const  $K$   
• reverse reaction

$$K' = \frac{1}{K} = K^{-1}$$

• multiply reaction  
by a factor  $n$

$$K'' = K^n$$

(b) Calculate  $K'$  for:  $\text{NH}_3 \rightleftharpoons \frac{3}{2}\text{H}_2 + \frac{1}{2}\text{N}_2$

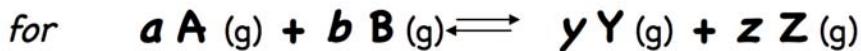
A. 
$$K' = \frac{[\text{H}_2]^{3/2} [\text{N}_2]^{1/2}}{[\text{NH}_3]} =$$

## Equilibria involving pressures

- for a gas, pressure and concentration are related by:

$$p = \left(\frac{n}{V}\right)RT = cRT \quad (c = \text{concentration})$$

- equilibrium constants for **gas phase reactions** can therefore be written in terms of equilibrium partial pressures:



$$K_p = \frac{(p_Y/p^\circ)^y (p_Z/p^\circ)^z}{(p_A/p^\circ)^a (p_B/p^\circ)^b}$$

$(p_z = \text{partial pressure of gas } Z;$   
 $p^\circ = \text{standard pressure} = 1.0 \times 10^5 \text{ Pa}$   
 $= 1.0 \text{ bar})$

$$= K_c (RT/p^\circ)^{\Delta n_{\text{gas}}}$$

{  $K_c$  = equil<sup>m</sup> constant in terms of concentrations (sometimes just written  $K$ );

$$\Delta n_{\text{gas}} = \sum(\text{product gas coefficients}) - \sum(\text{reactant gas coefficients})$$
$$= (y + z) - (a + b)$$

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## Relationship between $K_p$ and $K_c$

$$K_p = K_c \left( \frac{RT}{P^\circ} \right)^{\Delta n_g}$$

$\Delta n_g = (\text{moles of gaseous products}) - (\text{moles of gaseous reactants})$

Important to use correct units in this equation  
(the units for  $RT/p^\circ$  should cancel, so both sides are unitless)

# Solving equilibrium problems

[Blackman 9.5]

The equilibrium concentrations are linked through the reaction stoichiometry and the equilibrium constant

General method...

1. balance the reaction equation

2. concentration table

– write initial concentrations (or partial pressures)

– write changes required to reach equilibrium concentrations  
(if unknown, choose one change as  $x$ ; express others in terms of  $x$ ;  
increases in concentration are positive, decreases are negative)

– write equilibrium concentrations  
( = initial concentrations + changes)

3. substitute equilibrium concentrations into  
the equilibrium constant expression

4. solve unknown quantity

5. answer the question !!

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# Calculating equilibrium constants

FEEDBACK Example question

Q. When the reaction of 0.800 mol/L  $H_2$  and 0.500 mol/L  $N_2$  reaches equilibrium at a certain temperature, the concentration of the ammonia produced is 0.150 mol/L. Calculate the equilibrium constant.

A.

reaction equation & concentration table

	3 $H_2$	+	$N_2$	$\rightleftharpoons$	2 $NH_3$
initial	0.800		0.500		0
change	$- \frac{3}{2}(0.150)$		$-\frac{1}{2}(0.150)$		$+0.150$
equilibrium	0.575		0.425		0.150

substitute into the equilibrium constant expression and solve

$$K = \frac{[NH_3]^2}{[H_2]^3 [N_2]}$$

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# Calculating equilibrium concentrations #1

**FEEDBACK** Example question. Q. For a synthesis of hydrogen fluoride, 3.00 mol of  $H_2$  and 6.00 mol of  $F_2$  are mixed in a 3.00 L flask at a particular temperature. If the equilibrium constant for the synthesis reaction is  $1.15 \times 10^2$ , what are the equilibrium concentrations?

A. Solution:

reaction equation & concentration table

	$H_2$ (g)	+	$F_2$ (g)	$\rightleftharpoons$	2 $HF$ (g)
initial	3.00 mol / 3.00 L		6.00 mol / 3.00 L		0
	= 1.00		= 2.00		
change	-x		-x		+2x
equilibrium					

substitute into the equilibrium constant expression and solve

$$K = \frac{[HF]^2}{[H_2][F_2]} =$$

Cont'd...

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from previous slide ~

$$K = \frac{[HF]^2}{[H_2][F_2]} = \frac{(2x)^2}{(1.00 - x)(2.00 - x)} = 1.15 \times 10^2$$

∴

∴

∴

solve for x using the quadratic formula gives

$$x = 2.14 \text{ mol/L} \quad \text{and} \quad \underline{x} =$$

↑  
not real

( gives a physically impossible  $[H_2]$  )

substitute for x in table, gives

$$[H_2] =$$

$$[F_2] =$$

$$[HF] =$$

for the roots of a quadratic equation  
 $a x^2 + b x + c = 0$

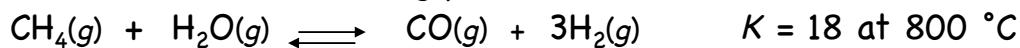
use the quadratic formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

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## Calculating equilibrium concentrations (or pressures) #2

**FEEDBACK** Example question. The majority of industrial hydrogen is produced by the steam reforming process:



Calculate (a)  $K_p$  and (b) the equilibrium partial pressures of all species if the partial pressures of steam and methane were 15 atm at the start.

A. Solution:

$$(a) K_p = K_c (RT/p^\circ)^{\Delta n_{\text{gas}}} = 18 (0.0821 \times (800 + 273)/1)^2 \quad \text{as } \Delta n_{\text{gas}} = 4 - 2 = 2 \\ = 1.4 \times 10^5$$

(b) write equilibrium equation & table

	$\text{CH}_4(g)$	$+$	$\text{H}_2\text{O}(g)$	$\rightleftharpoons$	$\text{CO}(g)$	$+$	$3\text{H}_2(g)$
initial (atm)	15		15		0		0
change (atm)	$-x$		$-x$		$+x$		$+3x$
equilibrium (atm)	$15 - x$		$15 - x$		$x$		$3x$

from previous slide ~

substitute into the equilibrium expression and solve

$$K_p = \frac{P_{\text{CO}} \cdot (P_{\text{H}_2})^3}{P_{\text{CH}_4} \cdot P_{\text{H}_2\text{O}}} = \frac{(x)(3x)^3}{(15 - x)(15 - x)} = \frac{27x^4}{(15 - x)^2} = 1.4 \times 10^5$$

take square roots of both sides

∴

solve for  $x$  using the quadratic formula

$$x = \quad (\text{the other solution for } x \text{ is negative and physically impossible})$$

at equilibrium, the pressures are

$$P_{\text{CH}_4} =$$

$$P_{\text{CO}} =$$

$$P_{\text{H}_2\text{O}} =$$

$$P_{\text{H}_2} =$$

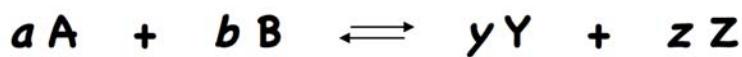
# Reaction quotients

[Blackman 9.4]

Is a chemical system at equilibrium?

For a general system that is **not necessarily at equilibrium**:

L2



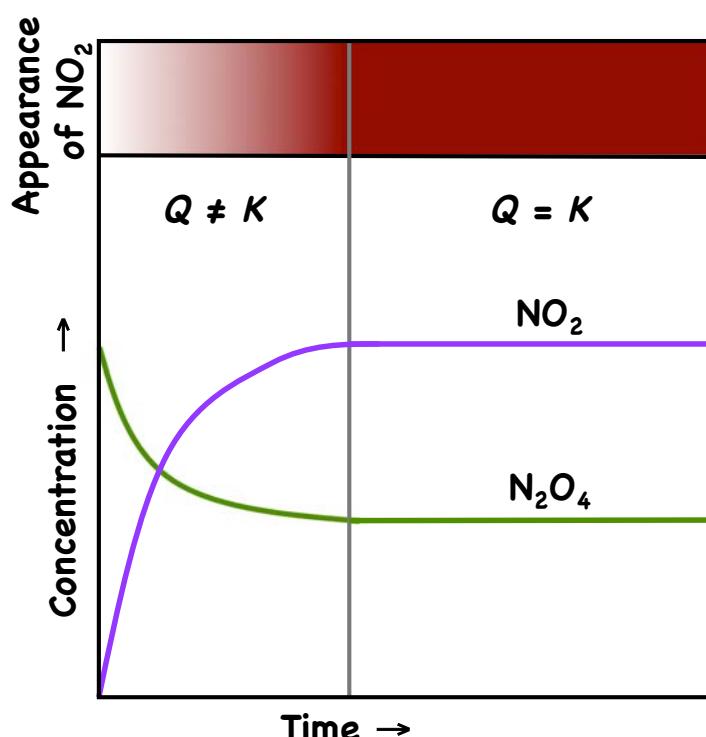
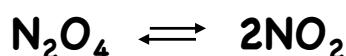
$$Q = \frac{[Y]^y [Z]^z}{[A]^a [B]^b}$$

calculated using the **initial concentrations** is called the **reaction quotient**

- $Q_c$  – reaction quotient
- Expression for systems not necessarily at equilibrium
- $K_c$  can have only one positive value at a specific temperature
- $Q_c$  can have any positive value
- At equilibrium:  $Q_c = K_c$

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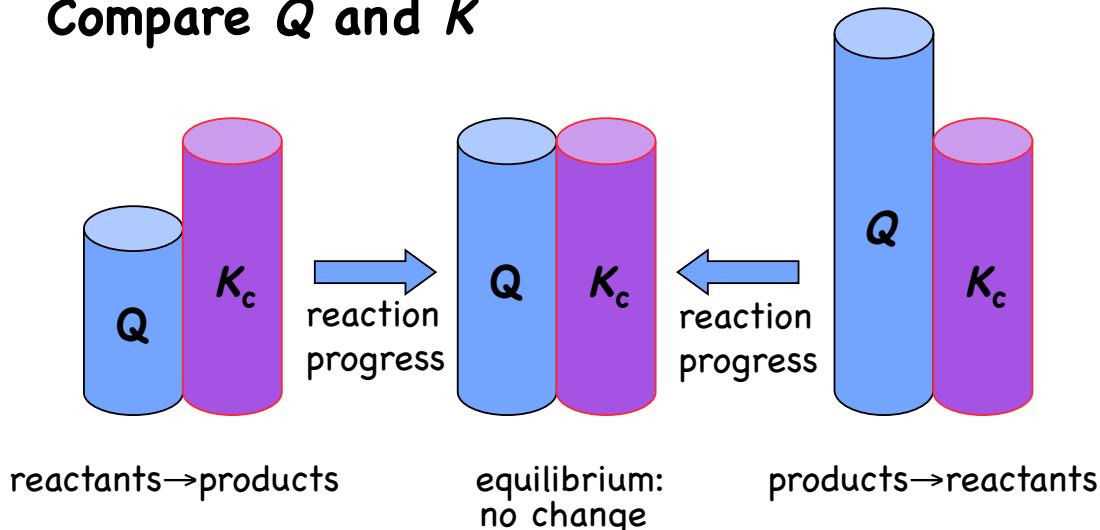
## Change in Q



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# Is a Chemical System at Equilibrium?

## Reaction Direction? Compare $Q$ and $K$

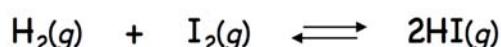


- $Q = K$ ; the system is **at equilibrium**; no net reaction will occur
- $Q < K$ ; **reactants → products** until equilibrium is reached
- $Q > K$ ; **products → reactants** until equilibrium is reached

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## Using reaction quotients

**FEEDBACK** Example question.  $Q$ : At 448 °C,  $K_c$  is 50.5 for the reaction



If a fixed volume vessel at 448 °C contains 20 mmol of HI, 10 mmol of  $H_2$  and 30 mmol of  $I_2$  is the system at equilibrium? If not, predict the direction in which the reaction will proceed.

### A. Solution

**starting concentrations:**  $[HI] = 2.0 \times 10^{-2} \text{ mol/V L}$

$$[H_2] = 1.0 \times 10^{-2} \text{ mol/V L}$$

$$[I_2] = 3.0 \times 10^{-2} \text{ mol/V L}$$

(where V = unknown vol. of vessel)

**reaction quotient:**

$$Q = \frac{[HI]^2}{[H_2][I_2]} = \underline{\hspace{2cm}} = 1.3 < K_c$$

V's cancel

∴ the  $[HI]$  is lower and the  $[H_2]$  and  $[I_2]$  higher than at equilibrium;  
→ net reaction will occur to raise  $[HI]$  relative to  $[H_2]$  and  $[I_2]$ ;  
ie. reaction occurs left to right →

## **Le Châtelier's Principle**

a chemical system, when perturbed from equilibrium,  
will react to re-establish equilibrium

... $K(T)$  is a CONSTANT

- If an outside influence upsets an equilibrium, the system undergoes a change in a direction that counteracts the disturbing influence and, if possible, returns the system to equilibrium

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## **Henri Louis Le Châtelier**



1850 - 1936

"He stressed the importance of discipline which his parents had imposed upon him .... He deplored the decreasing seriousness of study and the increasing tendency toward pleasure and even license in modern colleges and universities. He likened the irresponsible student to a bold individual who dodges vehicles in crossing a street and risks being crushed, to say nothing of the fact that he seriously ties up traffic..."

*Selected Readings in the History of Chemistry, Division of Chemical Education, American Chemical Society, Easton, PA, 1966, p. 142.*

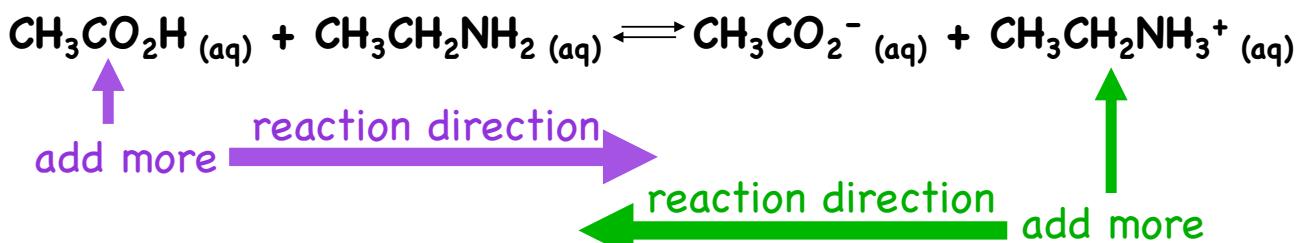
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# Le Chatelier's Principle –

a chemical system, when perturbed from equilibrium,  
will react to re-establish equilibrium

- add more of a reactant  $\Rightarrow$  reaction to produce more products
  - add more of a product  $\Rightarrow$  reaction to produce more reactants
- $K(T)$  is CONSTANT

Example. An aqueous solution of ethylamine (a weak base) and acetic acid:

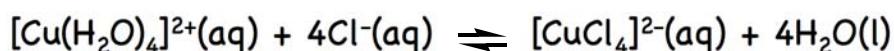


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## Response to change

a chemical system, when perturbed from equilibrium,  
will react to re-establish equilibrium

- Adding or removing a product or reactant
  - $Q = K$  equilibrium
  - $Q < K$  shift towards products
  - $Q > K$  shift towards reactants



$$Q = \frac{[\text{CuCl}_4^{2-}]}{[\text{Cu}(\text{OH}_2)_4^{2+}] [\text{Cl}^-]^4}$$

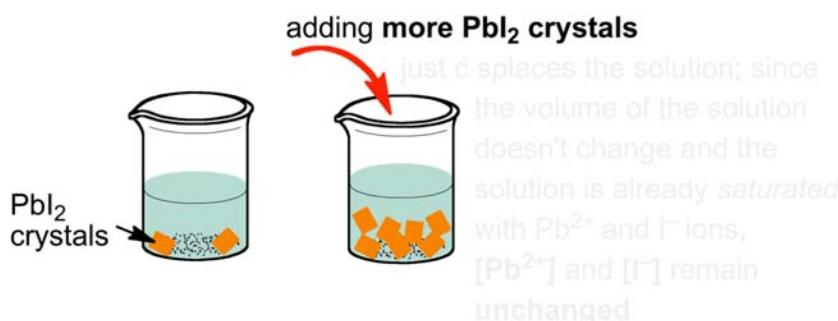
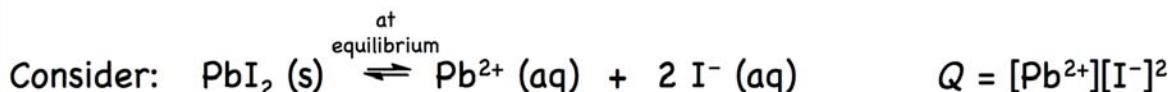


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## Response to change

a chemical system, when perturbed from equilibrium, will react to re-establish equilibrium

- Adding or removing a product or reactant that is a pure solid or pure liquid does NOT perturb a system that is at equilibrium (i.e. the amount of these has no effect)



## Response to change – gases

Changing the pressure in reactions involving gases

- $Q_p = K_p$  equilibrium
- $Q_p < K_p$  shift towards products
- $Q_p > K_p$  shift towards reactants

$$K_p = K_c \left( \frac{RT}{P^\theta} \right)^{\Delta n_g}$$

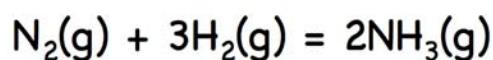
- Adding an inert gas has no effect
- At constant volume:
  - adding more reactant gas causes reaction to give more products
  - adding more product gas causes reaction to give more reactants
- Decreasing the volume – favours the side of the reaction with the least gas molecules
- Increasing the volume – favours the side of the reaction with the most gas molecules

## Response to change – gases

### Example question

### FEEDBACK – test your understanding

Q. Consider the following equilibrium in a closed piston kept at constant temperature:



$$Q_p = \frac{\left(\frac{P_{\text{NH}_3}}{P^\theta}\right)^2}{\left(\frac{P_{\text{N}_2}}{P^\theta}\right)\left(\frac{P_{\text{H}_2}}{P^\theta}\right)^3}$$

A. In lectures ...

What will be the effect of –

adding more ammonia at const. volume : .....

adding more hydrogen at const. volume : .....

adding helium at const. volume : .....

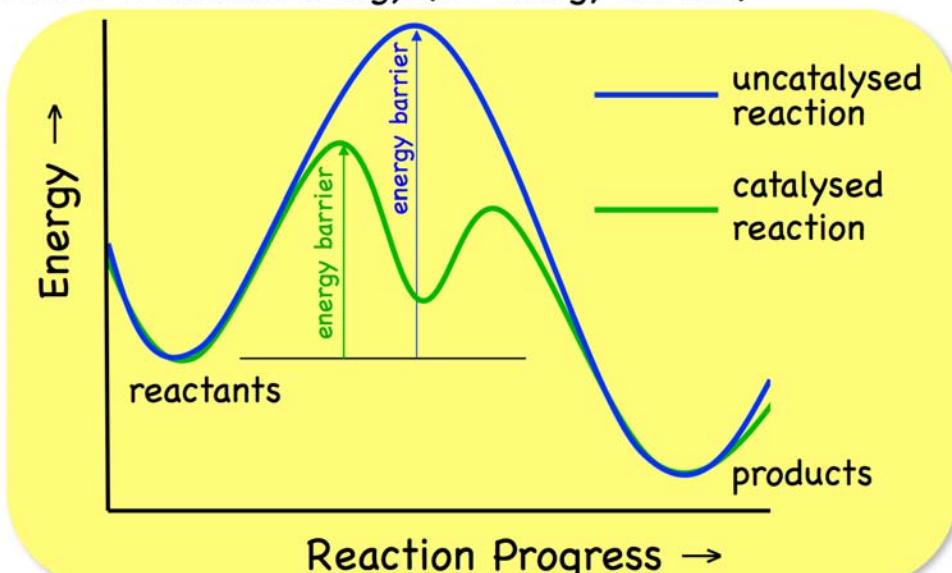
decreasing the volume : .....

expanding the piston by adding helium to  
keep the total pressure constant : .....

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## Effect of a catalyst

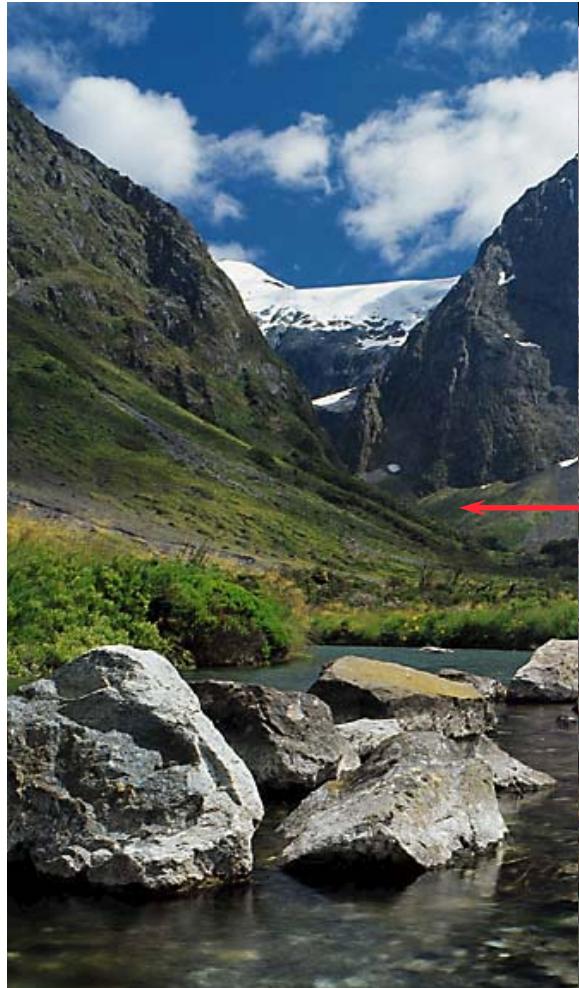
- add catalyst – no change
  - a catalyst only affects the rate of reaction, not the final concentrations
  - a catalyst provides an alternative pathway for a reaction with a lower *activation energy* (*i.e.* energy barrier)



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before the Homer tunnel...  
(began 1930's, road opened 1954)  
**high barrier** ⇒ FEW tourists



Now, each year, >600,000 tourists...  
**low barrier** ⇒ MANY tourists



## Response to change – temperature

- Changing the temperature of a reaction mixture
- Consider  $aA + bB \rightleftharpoons yY + zZ + \text{heat}$  (exothermic)  
or  $aA + bB + \text{heat} \rightleftharpoons yY + zZ$  (endothermic)

Exothermic: heat is given out by the reaction ( $\Delta_rH^\circ$  is negative \*)

Endothermic: heat is taken up by the reaction ( $\Delta_rH^\circ$  is positive \*)

Adding heat:

Exothermic

$$Q > K$$

Reactants are favoured

Endothermic

$$Q < K$$

Products are favoured

\* Standard enthalpy of reaction, which corresponds to the heat of reaction at constant pressure (coming up in lectures soon!)

## Response to change – temperature & K

- Changing the temperature changes the equilibrium constant (K)
- Consider  $aA + bB \rightleftharpoons cC + dD + \text{heat}$  ( $\Delta_rH^\circ < 0$ )  
or  $aA + bB + \text{heat} \rightleftharpoons cC + dD$  ( $\Delta_rH^\circ > 0$ )

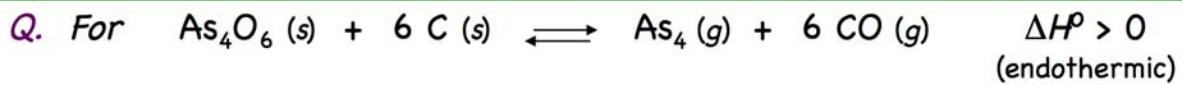
Can use the **van't Hoff equation** to calculate the K at a specified temperature if the value of K at another temperature and the value of  $\Delta_rH^\circ$  is known:

$$\ln K_{T_2} - \ln K_{T_1} = \frac{\Delta_rH^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

**Do not learn this – it will be given if needed**

\* Standard enthalpy of reaction, which corresponds to the heat of reaction at constant pressure (coming up in lectures soon!)

# Using Le Chatelier's Principle



use Le Châtelier's Principle to predict how the following changes will affect a system initially at equilibrium:

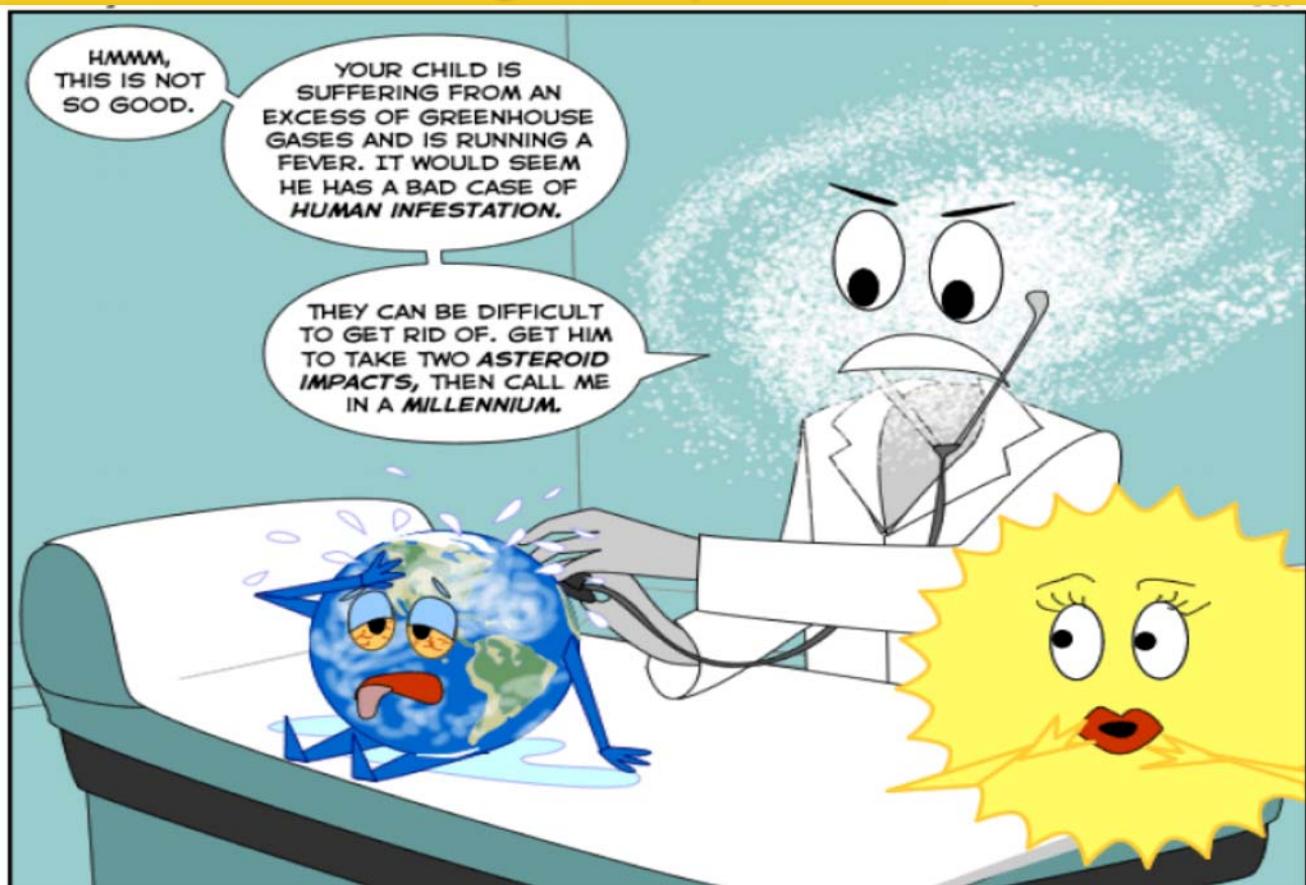
change	moles $\text{As}_4$ *	$K$
Add $\text{As}_4\text{O}_6$		
Add C		
Add CO		
Remove $\text{As}_4$		
Add He (g)		
Add catalyst		
Decrease volume		
Increase volume		
Decrease temperature		
Increase temperature		

## FEEDBACK

\* total moles of  $\text{As}_4$  produced by the reaction

think critically,  
test yourself

## "Life on Earth" and global equilibrium



# How should I study for this topic?

**THINK CRITICALLY!!**

Ask yourself: **Do I understand** everything presented? Can I do all the problems... from lectures, worksheets & tutes?

Try to understand the material...  
(use the syllabus & lectures as a guide)

Attend **lectures**, do **worksheets**...

Read **lecture notes** & **textbook** ...

Do some more problems ...  
(from **tutorials**, **textbook** & **sample exams**)

Do some more problems ...

*repeat till you  
understand it all!!*

