

Slide 1

**Thermodynamic  
Connection**

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Q and G and letters other than  
K

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Slide 2

**Reaction Quotient**

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What do you call an equilibrium constant when you aren't at equilibrium?

A Reaction Quotient! (Q)

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Slide 3

**Consider...**

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1 mole of Hydrogen, 2 moles of Oxygen, and 1 mole of water are mixed in a 2 L flask at 800 K. The equilibrium constant for the formation of steam at 800 K is  $1.6 \times 10^{-6}$ . Find the equilibrium concentrations...yada yada yada

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### Slide 4

Let's just set it up

$2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2 \text{H}_2\text{O}(\text{g})$

Initial	1 mol/2L	2 mol/2L	1 mol/2L
Change	0.5 M	1 M	0.5 M
Equilibrium			

M is preferable if I'm going to solve the K expression for [equilibrium]

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### Slide 5

Let's just set it up

$2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2 \text{H}_2\text{O}(\text{g})$

Initial	0.5 M	1 M	0.5 M
Change	-2 x	-x	+ 2 x
Equilibrium	???	???	???

We don't need to know the sign, it'll all come out in the solution, but is there a way to know???

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### Slide 6

Q tells us where we are

$Q = \frac{\text{[products NOT at equilibrium]}}{\text{[reactants NOT at equilibrium]}}$

In this case:

$$Q = \frac{[\text{H}_2\text{O}]^2}{[\text{H}_2]^2[\text{O}_2]} = \frac{(0.5 \text{ M})^2}{(0.5 \text{ M})^2(1 \text{ M})} = 1$$

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Slide 7

What does the “Q=1” mean?

How should we evaluate Q?

Q is just K when I haven't gotten to K, so Q is trying to become K.

Compare Q to K

$K = 1.6 \times 10^{-6}$  at this temperature

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Slide 8

$Q=1, K=1.6 \times 10^{-6}$

A The reaction needs to go right to get to equilibrium

B. The reaction needs to go left

C. The reaction is at equilibrium

D. I don't care because I don't want to justify my answer

E. I'm sleeping.

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Slide 9

Q = 1

$K = 1.6 \times 10^{-6}$

Q is too BIG...

Q =  $\frac{[\text{products}]}{[\text{reactants}]}$  [products] is too big!

Reaction must go left to get rid of the products to reach equilibrium.

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Slide 10

Q vs. K

If  $Q > K$ , too many products, reaction goes left.

If  $Q < K$ , too many reactants (too few products), reaction goes right.

If  $Q = K$ ...everything is just right!

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Slide 11

Too many products, so...

$2 \text{H}_2 (\text{g}) + \text{O}_2 (\text{g}) \leftrightarrow 2 \text{H}_2\text{O} (\text{g})$

Initial	0.5 M	1 M	0.5 M
Change	+2x	+ x	-2x
Equilibrium			

So, we can determine the sign of the change if we want to!

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Slide 12

K in context

We've talked about a number of different realms of Chemistry.

1. Kinetics – How fast?
2. Thermodynamics – How stable? How hot?
3. Equilibrium...???

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Slide 13

Equilibrium and Thermodynamics

Would it surprise you to know that Equilibrium represents the thermodynamic balance between the products and the reactants?

Equilibrium tells us what the balance should be, but says nothing about how fast (kinetics) it takes to get there.

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Slide 14

Gibbs Free Energy

Gibbs Free Energy is the most important thermodynamic variable: it balances enthalpy and entropy.

$\Delta G = \Delta H - T \Delta S$

If  $\Delta G < 0$ , what does that mean?  
Reaction is spontaneous as written.

If  $\Delta G > 0$ , what does that mean?  
Reaction is spontaneous in the reverse direction.

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Slide 15

$\Delta G$  sounds a lot like Q!

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Slide 16

K (Q) is related to  $\Delta G$

If  $\Delta G < 0$ , reaction is spontaneous as written (to right).

If  $\Delta G > 0$ , reaction is spontaneous in the reverse direction (to left).

If  $Q > K$ , reaction goes left.

If  $Q < K$ , reaction goes right.

If  $Q = K$ , we're at equilibrium. At equilibrium,  $\Delta G = 0!!!$

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Slide 17

As a reaction proceeds, what happens...

You make products from reactants (or make reactants from products) until equilibrium is reached.

Assume  $Q < K$ , what does that mean?

Reaction wants to go right. So  $\Delta G...?$   
 $\Delta G < 0$

Eventually, you reach equilibrium,  $Q = K$ .  $\Delta G = 0$

$\Delta G$  must depend on concentration!!!

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Slide 18

$\Delta G$  is "naught'y"

What's the difference between  $\Delta G$  and  $\Delta G^\circ$ ?

$\Delta G^\circ$  is at standard conditions:

1. 298 K
2. 1 atm
3. Stoichiometric quantities of everything (1 M aqueous, 1 atm gases)

$\Delta G$  is at any arbitrary conditions

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Slide 22

**Sample Problem**

What is the equilibrium problem for the following reaction at 250 °C?

$$\text{CO}_{(g)} + 2 \text{H}_2_{(g)} \leftrightarrow \text{CH}_3\text{OH}_{(g)}$$
$$\Delta H^\circ = \Delta H_f^\circ (\text{products}) - \Delta H_f^\circ (\text{reactants})$$
$$= (-201.0 \text{ kJ}) - (-110.5 \text{ kJ} + 2(0))$$
$$= -90.5 \text{ kJ}$$
$$\Delta S^\circ = S_f^\circ (\text{products}) - S_f^\circ (\text{reactants})$$
$$= (239.9 \text{ J/K}) - (197.7 \text{ J/K} + 2(130.7 \text{ J/K}))$$
$$= -219.2 \text{ J/K}$$

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Slide 23

**Sample Problem**

What is the equilibrium problem for the following reaction at 250 °C?

$$\text{CO}_{(g)} + 2 \text{H}_2_{(g)} \leftrightarrow \text{CH}_3\text{OH}_{(g)}$$
$$\Delta H^\circ - T\Delta S^\circ = -RT \ln K$$
$$-90.5 \text{ kJ} - ((250 + 273.15)K) \left( -219.2 \frac{\text{J}}{\text{K}} \right) = -RT \ln K$$
$$24,174.5 = - \left( 8.314 \frac{\text{J}}{\text{molK}} \right) (523.15 \text{ K}) \ln K$$

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Slide 24

**Sample Problem**

What is the equilibrium problem for the following reaction at 250 °C?

$$\text{CO}_{(g)} + 2 \text{H}_2_{(g)} \leftrightarrow \text{CH}_3\text{OH}_{(g)}$$
$$24,174.5 = - \left( 8.314 \frac{\text{J}}{\text{molK}} \right) (523.15 \text{ K}) \ln K$$
$$-5.56 = \ln K$$
$$K = e^{-5.56} = 3.85 \times 10^{-3}$$

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Slide 25

**Clicker Question**

What is the K for our favorite reaction at 25° C:  
 $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2 \text{H}_2\text{O}(\text{g})$

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Slide 26

Substance	$\Delta H_f^\circ$ (kJ/mol)	$\Delta G_f^\circ$ (kJ/mol)	$S^\circ$ (J/mol·K)
H(g)	218.0	203.3	114.7
H <sup>+</sup> (aq)	0	0	0
H <sup>-</sup> (g)	1536.3	1517.1	108.9
H <sub>2</sub> (g)	0	0	130.7
I(g)	106.76	70.2	180.79
HI(g)	26.5	1.7	206.6
OH <sup>-</sup> (aq)	-230.02	-157.3	-19.90
O(g)	249.2	231.7	161.1
O <sub>2</sub> (g)	0	0	205.2
O <sub>3</sub> (g)	142.7	163.2	238.9
H <sub>2</sub> O(l)	-285.8	-237.1	70
H <sub>2</sub> O(g)	-241.8	-228.6	188.8
H <sub>2</sub> O <sub>2</sub> (l)	-187.8	-120.4	109.6
H <sub>2</sub> O <sub>2</sub> (g)	-136.3	-105.6	232.7
N(g)	472.7	455.5	153.3
N <sub>2</sub> (g)	0	0	191.6
NH <sub>3</sub> (g)	-46	-16	193
NH <sub>3</sub> (aq)	-80.29	-26.50	111.3
NH <sub>4</sub> <sup>+</sup> (aq)	-133.26	-79.31	111.17
NO(g)	91.3	87.6	210.8
NO <sub>2</sub> (g)	33.2	51.3	240.1
N <sub>2</sub> O(g)	81.6	103.7	220.0
N <sub>2</sub> H <sub>4</sub> (g)	95.4	159.4	238.5
N <sub>2</sub> O <sub>4</sub> (g)	9.16	99.8	304.4

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Slide 27

$2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \leftrightarrow 2 \text{H}_2\text{O}(\text{g})$

$\Delta G^\circ = -RT \ln K$

$\Delta G^\circ = \sum \Delta G_f^\circ(\text{products}) - \sum \Delta G_f^\circ(\text{reactants})$

$$\Delta G^\circ = \left[ 2 \times \left( -228.6 \frac{\text{kJ}}{\text{mol}} \right) \right] - [2(0) + 0] = -457.2 \frac{\text{kJ}}{\text{mol}}$$

$$-457.2 \frac{\text{kJ}}{\text{mol}} = -RT \ln K$$

$$-457.2 \frac{\text{kJ}}{\text{mol}} = - \left( 8.314 \frac{\text{J}}{\text{molK}} \right) (298 \text{ K}) \ln K$$

$$-457.2 \times \frac{10^3 \text{ J}}{\text{mol}} = - \left( 8.314 \frac{\text{J}}{\text{molK}} \right) (298 \text{ K}) \ln K$$

$$184.52 = \ln K$$

$$K = e^{184.52} = 1.38 \times 10^{80}$$


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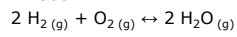
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Slide 28

### Clicker Question

What is the K for our favorite reaction at 1000 K:



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Slide 29

$$\begin{aligned} -457.2 \text{ kJ/mol} &= -RT \ln K \\ -457.2 \text{ kJ/mol} &= -(8.3145 \text{ J/mol K})(1000 \text{ K}) \ln K \\ -457.2 \times 10^3 \text{ J/mol} &= -(8.3145 \text{ J/mol K})(1000 \text{ K}) \ln K \\ 54.988 &= \ln K \\ K &= e^{54.988} = 7.6 \times 10^{23} \end{aligned}$$

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Slide 30

### Le Chatelier's Principle

It's FRENCH! (Very classy!)

Uncle Joe's stress management hints!

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Slide 31

1 atm O<sub>2</sub>, 0.5 atm H<sub>2</sub> and 0.1 atm of H<sub>2</sub>O  
are mixed.

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Slide 32

If I shove you, what do you do?

- A. Shove back
- B. Step back and absorb the blow
- C. Get a gun and escalate the fight
- D. Cry

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Slide 33

If I shove you, what do you do?

- A. Shove back (Yeah, right!)
- B. Step back and absorb the blow (NICE!)
- C. Get a gun and escalate the fight  
(Seriously, ruin your life over a shove.)
- D. Cry (Probably...but not constructive.)

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Slide 34

In fact, the best move...  
...roll with the shove.

THAT is Le Chatelier's principle: A system under stress responds to alleviate the stress.

Equilibrium reactions are constantly going in both directions. If you stress the reaction in any way, the reactions respond to the stress.

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Slide 35

If I turn down the thermostat in here to 40 degrees, what do you do?

You are cold you need to get heat.

How would a reaction get heat?

One reaction is EXOthermic, one is ENDOthermic. If you turn down the thermostat, the reaction just turns up its thermostat!

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Slide 36

If you turn down T...  
...you favor the exothermic reaction.

The equilibrium shifts to relieve the stress.

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Slide 37

If you turn up the heat...

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...you favor the endothermic reaction (absorbing heat).

The equilibrium shifts to accommodate the stress.

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Slide 38

$2 \text{H}_2 + \text{O}_2 \leftrightarrow 2 \text{H}_2\text{O}$

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If I add hydrogen, what does the reaction do?

Make more water to use up the hydrogen!

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Slide 39

$2 \text{H}_2 + \text{O}_2 \leftrightarrow 2 \text{H}_2\text{O}$

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$2 \text{H}_2 + \text{O}_2 \leftrightarrow 2 \text{H}_2\text{O}$

E	2 mol	2 mol	5 mol
stress	+1 mol		
I	3 mol	2 mol	5 mol

You've upset the equilibrium!

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Slide 40

$2 \text{H}_2 + \text{O}_2 \leftrightarrow 2 \text{H}_2\text{O}$

If I remove water from the system, what does the reaction do?

Make more water!

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Slide 41

$2 \text{H}_2 + \text{O}_2 \leftrightarrow 2 \text{H}_2\text{O}$

$2 \text{H}_2 + \text{O}_2 \leftrightarrow 2 \text{H}_2\text{O}$

E	2 mol	2 mol	5 mol
stress			-3 mol
1	2 mol	2 mol	2 mol

You've upset the equilibrium!  
 $\Delta G = \Delta G^\circ + RT \ln Q$   
You were at  $\Delta G=0, Q=K$

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Slide 42

$2 \text{H}_2 (\text{g}) + \text{O}_2 (\text{g}) \leftrightarrow 2 \text{H}_2\text{O} (\text{g})$

Suppose you increase the Pressure!!!

The reaction makes itself "small"...shifts to the right. 2 moles of water takes up less space than 3 moles of reactants IF they are all gases.

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Slide 43

$H_2O (s) \leftrightarrow H_2O (l)$

- A. Left
- B. Right
- C. No effect

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Slide 44

The test ends here...

Topics for the test:

- 1. Titration curves
  - 1. Strong acid/strong base
  - 2. Weak acid/strong base or strong acid/weak base
  - 3. Buffers
  - 4. Salts
  - 5. Ka or Kb or Kw
- Soup Problems – mixtures of stuff
  - 1. Ksp
    - 1. Solubility
    - 2. Fractional precipitation
  - 2. Thermodynamics
    - 1.  $\Delta H, \Delta S, \Delta G$
    - 2.  $\Delta G = \Delta H - T \Delta S$
    - 3.  $K (\Delta G = \Delta G^\circ + RT \ln Q)$

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Slide 45

Don't forget

Exam review homework is due at **8**  
**p.m.** on Thursday.

Complete solutions for exam review homework appear magically on myCourses under "Content" at 9:01 p.m. on Wednesday.

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