# Lecture 13 CH131 Summer 1

Wednesday, June 12, 2019

- Example problems
- Effect of temperature on spontaneity

Begin ch14: Chemical equilibrium

- Reaction quotient, spontaneity, and equilibrium

Next lecture: Continue ch14

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## Problem 7e and 8e 13.31

**31.** Ethanol's enthalpy of vaporization is 38.7 kJ mol$^{-1}$ at its normal boiling point, 78°C. Calculate $q$, $w$, $\Delta U$, $\Delta S_{sys}$, and $\Delta G$ when 1.00 mol ethanol is vaporized reversibly at 78°C and 1 atm. Assume that the vapor is an ideal gas and neglect the volume of liquid ethanol relative to that of its vapor.

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Effect of temperature on spontaneity

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## Atomic or molecular oxygen?

At what temperature will oxygen spontaneously decompose, $O_2(g) \to 2\ O(g)$?

- $\Delta H_f(O, g) = 249.2$ kJ/mol
- $S°(O, g) = 161.1$ J/(K mol)
- $S°(O_2, g) = 205.0$ J/(K mol)

How to proceed?

At 300 K,

$\Delta G = 2 \times 249.2 - 300\ \text{K} \times 10^{-3}(2 \times 161.1 - 205.0) = +463$ kJ

Since > 0, not spontaneous, so mostly molecules at 300 K

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## Atomic or molecular oxygen?

At what temperature will oxygen spontaneously decompose, $O_2(g) \rightarrow 2\ O(g)$?

At 300 K,

$$\Delta G = 2 \times 249.2 - 300\ \text{K} \times 10^{-3}(2 \times 161.1 - 205.0) = +463\ \text{kJ}$$

At what $T$ will decomposition become spontaneous?

$$\Delta G = 0 = 2 \times 249.2 - T \times 10^{-3}(2 \cdot \times 161.1 - 205.0)$$

$$T = 2 \cdot 249.2 \times 10^3/(2 \times 161.1 - 205.0) = 4253\ \text{K}$$

So, for $T$ above 4253 K, mostly atoms

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## Atomic or molecular oxygen?

At what temperature will oxygen spontaneously decompose, $O_2(g) \rightarrow 2\ O(g)$?

OK, we have seen that

- at low $T$ oxygen is mostly molecules,
- but at high $T$ it is mostly atoms.

Why?

Even though breaking the molecule apart raises the entropy of the system, it takes energy from surroundings to break bonds and so entropy of surroundings is lowered.

But, high temperature mutes lowering of $S_{sur}$.

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[TP] A certain chemical reaction is not spontaneous at 300 K. The entropy change for the reaction is +130 J/K. The reaction must be ...

100% 1. endothermic
0% 2. exothermic
0% 3. neither ($\Delta H = 0$)
0% 4. More information needed

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[TP] At 300 K, hydrogen and oxygen react explosively to form water. The free energy of formation of water is −237 kJ. Based on this information, at very high temperature, water will ...

71% 1. decompose into $H_2$ and $O_2$
24% 2. will not decompose into $H_2$ and $O_2$
6% 3. More information needed

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## $\Delta G$ versus $T$

$\Delta G = \Delta H - T\,\Delta S = b + m\,x$

Intercept $b = \Delta H$, slope $m = -\Delta S$, $x = T$

Sketch the four families of lines $\Delta G$ versus $T$, distinguished by the signs of $b$ and of $m$.

1. $b = \Delta H > 0$ slope $m = -\Delta S < 0$
2. $b = \Delta H > 0$ slope $m = -\Delta S > 0$
3. $b = \Delta H < 0$ slope $m = -\Delta S < 0$
4. $b = \Delta H < 0$ slope $m = -\Delta S > 0$

Which family corresponds to $H_2$ burning in air?

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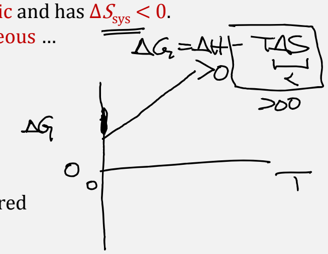
[Quiz] A chemical reaction is endothermic and has $\Delta S_{sys} < 0$.
This means the reaction will be spontaneous ...

| | | |
|---|---|---|
| 35% | 1. | only at low temperature |
| 12% | 2. | only at high temperature |
| 6% | 3. | always |
| 47% | 4. | never |
| 0% | 5. | Further information required |



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Begin ch14: Chemical equilibrium

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## Spontaneity of "reactants" → "products"

If products (right side) increase with time, we say the reaction is spontaneous.

If reactants (left side) increase with time, we say the reaction is nonspontaneous.

If the amount of reactants and products do not change with time, we say the reaction is at equilibrium.

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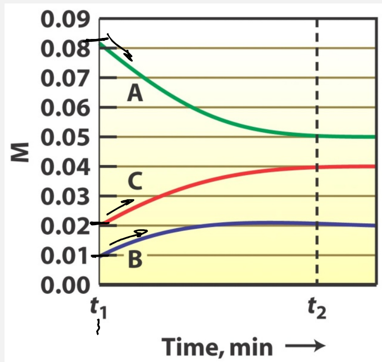
## Spontaneous approach to equilibrium: A → B + C

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## Reaction quotient *Q* measures progress

A → B + C

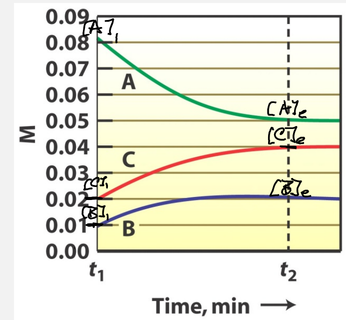
$Q$ = products/reactants = [B][C]/[A]

$Q$ at $t_1$ is smaller

$Q$ at $t_2$ is larger

$Q$ thereafter no longer changes

For $t > t_2$, $Q = K$, equilibrium constant

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## Reaction quotient *Q* measures progress

For A → B + C, the reaction quotient is …

$Q = [B][C]/[A]$

The numerical value of the reaction quotient when the concentrations have their equilibrium values …

$[A]_e$, $[B]_e$ and $[C]_e$

and so no longer change with time, is called the equilibrium constant …

$K = [B]_e[C]_e/[A]_e$

$Q = \frac{[B][C]}{[A]}$

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## Practice: Problem 14.5

**5.** An important step in the industrial production of hydrogen is the reaction of carbon monoxide with water:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

**(a)** Use the law of mass action to write the equilibrium expression for this reaction.

**(b)** At 500°C, the equilibrium constant for this reaction is 3.9. Suppose that the equilibrium partial pressures of CO and $H_2O$ are both 0.10 atm and that of $CO_2$ is 0.70 atm. Calculate the equilibrium partial pressure of $H_2(g)$.

$K = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} = 3.9$

| CO | $H_2O$ | $CO_2$ | $H_2$ |
|---|---|---|---|
| 0.10 | 0.10 | 0.70 | |

$K = \frac{0.70 \times P_{H_2}}{(0.10)(0.10)} = 3.9$

$P_{H_2} = \frac{3.9 \times 0.01}{0.70} =$

$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

$K = \frac{(P_{H_2O})^2}{(P_{H_2})^2 P_{O_2}}$

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## Practice: Problem 14.11

**11.** Using the law of mass action, write the equilibrium expression for each of the following reactions.

(a) $Zn(s) + 2\ Ag^{+}(aq) \rightleftharpoons Zn^{2+}(aq) + 2\ Ag(s)$

(b) $VO_4^{3-}(aq) + H_2O(\ell) \rightleftharpoons VO_3(OH)^{2-}(aq) + OH^{-}(aq)$

(c) $2\ As(OH)_6^{3-}(aq) + 6\ CO_2(g) \rightleftharpoons As_2O_3(s) + 6\ HCO_3^{-}(aq) + 3\ H_2O(\ell)$

a) $K = \dfrac{[Zn^{2+}]/1M\ ([Ag]/[Ag])}{([Ag^+]/1M)^2\ ([Zn]/[Zn])} = \dfrac{[Zn^{2+}]}{[Ag^+]^2}$

c) $K = \dfrac{[HCO_3^-]^6}{[As(OH)_6^{3-}]^2 (P_{CO_2})^6}$

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## *Q* versus *K* is the key to assessing spontaneity

If $Q < K$, product must form to get to equilibrium,
so spontaneous

If $Q > K$, reactants must form to get to equilibrium,
so nonspontaneous

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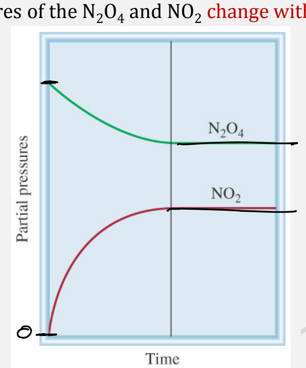
## $N_2O_4 \rightleftharpoons 2\ NO_2$

The figure shows how the partial pressures of the $N_2O_4$ and $NO_2$ change with time due to the chemical reaction

$$N_2O_4 \rightleftharpoons 2\ NO_2$$

for certain initial conditions.

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## $N_2O_4 \rightleftharpoons 2\ NO_2$

$P = \frac{n}{V}RT$

The reaction quotient is

$$Q = [NO_2]^2/[N_2O_4]$$

The numerical value of the reaction quotient when the concentrations have their equilibrium values

$$[N_2O_4]_e \text{ and } [NO_2]_e$$

and so no longer change with time, is called the equilibrium constant

$$K = [NO_2]_e^2/[N_2O_4]_e$$

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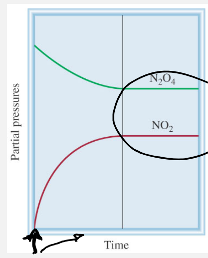
[TP] The figure shows how the partial pressures of the $N_2O_4$ and $NO_2$ change with time due to the chemical reaction

$N_2O_4 \rightleftharpoons 2\ NO_2$

for certain initial conditions. At these initial conditions, the following is known about the chemical reaction.

73% 1. It is spontaneous
7% 2. It is at equilibrium
0% 3. It is non-spontaneous
20% 4. Its spontaneity is not known without further information

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[TP] At the initial conditions for the reaction

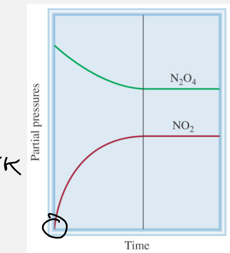
$N_2O_4 \rightleftharpoons 2\ NO_2$

the following is known about the ratio $Q/K$.

20% 1. It is greater than 1
7% 2. It is equal to 1
73% 3. It is less than 1
0% 4. The ratio is not known without further information

$Q = \frac{0}{\infty} = 0 < K$

$Q/K < 1$

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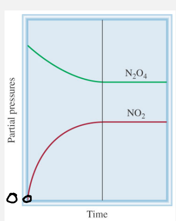
[TP] For the reaction

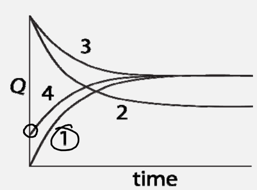
$N_2O_4 \rightleftharpoons 2\ NO_2$

which curve on the right shows the corresponding change of Q with time?

82% 1. 1
6% 2. 2
0% 3. 3
12% 4. 4
0% 5. None

$Q = 0$

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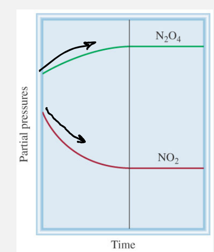
[Quiz] The figure shows how the partial pressures of the $N_2O_4$ and $NO_2$ change with time due to the chemical reaction

$N_2O_4 \rightleftharpoons 2\ NO_2$

for certain initial conditions. At these initial conditions, the following is known about the chemical reaction.

6% 1. It is spontaneous
0% 2. It is at equilibrium
94% 3. It is non-spontaneous
0% 4. Its spontaneity is not known without further information

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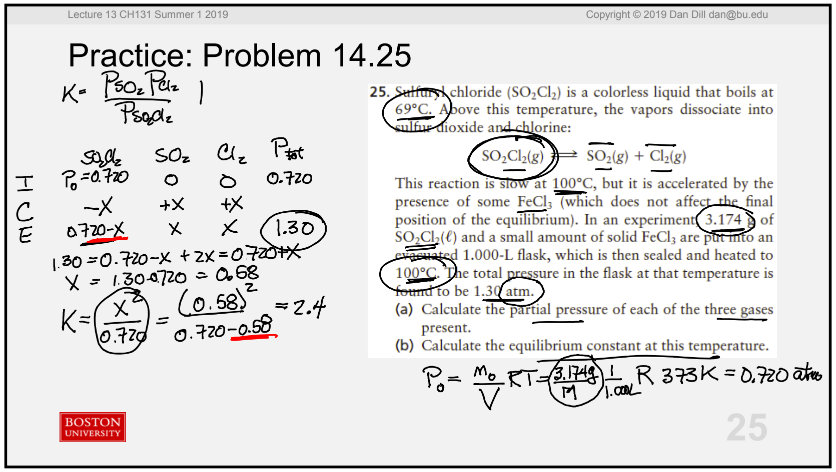
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Practice: Problem 14.25
25. Sulfuryl chloride ($SO_2Cl_2$) is a colorless liquid that boils at 69°C. Above this temperature, the vapors dissociate into sulfur dioxide and chlorine:
$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$
This reaction is slow at 100°C, but it is accelerated by the presence of some $FeCl_3$ (which does not affect the final position of the equilibrium). In an experiment 3.174 g of $SO_2Cl_2(\ell)$ and a small amount of solid $FeCl_3$ are put into an evacuated 1.000-L flask, which is then sealed and heated to 100°C. The total pressure in the flask at that temperature is found to be 1.30 atm.
(a) Calculate the partial pressure of each of the three gases present.
(b) Calculate the equilibrium constant at this temperature.
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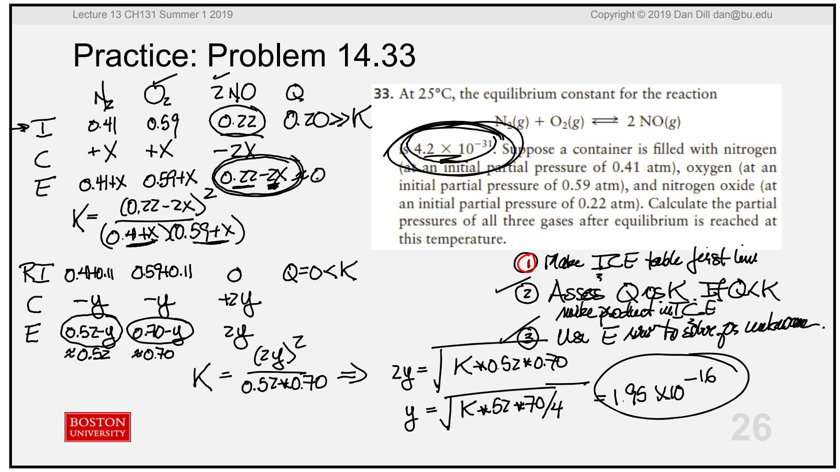
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Practice: Problem 14.33
33. At 25°C, the equilibrium constant for the reaction
$N_2(g) + O_2(g) \rightleftharpoons 2\ NO(g)$
is $4.2 \times 10^{-31}$. Suppose a container is filled with nitrogen (at an initial partial pressure of 0.41 atm), oxygen (at an initial partial pressure of 0.59 atm), and nitrogen oxide (at an initial partial pressure of 0.22 atm). Calculate the partial pressures of all three gases after equilibrium is reached at this temperature.
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