Lecture 13 CH131 Summer 1
Wednesday, June 17, 2020

- An alternative criterion of spontaneity: Free energy change, ΔG
- Example problems
- Effect of temperature on spontaneity

Begin ch14: Chemical equilibrium
- Reaction quotient, spontaneity, and equilibrium

Next lecture: Continue ch14

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An alternative criterion of spontaneity

Quantifying spontaneity, we have learned so far:

$$W \rightarrow S = k_B \ln(W) \rightarrow \Delta S = k_B \ln\left(\frac{W_f}{W_i}\right)$$

$$\Delta S_{\text{tot}} = \Delta S_{\text{sur}} + \Delta S_{\text{sys}}$$

$$\Delta S_{\text{sur}} = \frac{q_{\text{sur}}}{T} = -\frac{\Delta H_{\text{sys}}}{T}$$

$$\Delta S_{\text{tot}} = -\frac{\Delta H_{\text{sys}}}{T} + \Delta S_{\text{sys}}$$

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An alternative criterion of spontaneity

For phase transitions:

$$\Delta S_{\text{tot}} = -\frac{\Delta H_{\text{sys}}}{T} + \Delta S_{\text{sys}}$$

$$= -\frac{\Delta H_{\text{transition}}}{T} + \frac{\Delta H_{\text{transition}}}{T_{\text{transition}}}$$

$l \rightarrow g$
$T_{\text{transition}} = 100^\circ C$
T = actual temp.
$s \rightarrow l$
$T_{\text{transition}} = 0^\circ C$
$s \rightarrow g$
$T_{\text{transition}} = ?$

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An alternative criterion of spontaneity

For chemical reactions:

$$\Delta S_{\text{tot}} = -\frac{\Delta H_{\text{sys}}}{T} + \Delta S_{\text{sys}}$$

$$= -\frac{\Delta H_{\text{rxn}}}{T} + \Delta S_{\text{rxn}}$$

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[TP] While ΔS_{tot} takes into account entropy change in both the surroundings and the system, the expression $\Delta S_{\text{tot}} = -\frac{\Delta H_{\text{rxn}}}{T} + \Delta S_{\text{rxn}}$ means that for chemical reactions, ...

18% 1. the entropy change of the surroundings is not important
82% 2. then entropy change of the surroundings still plays a role
0% 3. only exothermic reactions are spontaneous
0% 4. Further information needed

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An alternative criterion of spontaneity

While the expression

$$\Delta S_{\text{tot}} = -\frac{\Delta H_{\text{rxn}}}{T} + \Delta S_{\text{rxn}}$$

has only properties of the system, always remember that $-\frac{\Delta H_{\text{rxn}}}{T}$ is the entropy change of the surroundings.

This shows that spontaneity is favored by exothermic reactions ($\Delta H_{\text{rxn}} < 0$) because they increase the entropy of the surroundings.

However, whether a reaction is spontaneous ($\Delta S_{\text{tot}} > 0$) also depends on ΔS_{rxn}.

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Free energy change, ΔG

To emphasize that we only have to know the system quantities ΔH_{rxn} and ΔS_{rxn} , the free energy change of reaction is defined as

$$-T\Delta S_{\text{tot}} = \Delta G_{\text{rxn}} = \Delta H_{\text{rxn}} - T\Delta S_{\text{rxn}}$$

The components of ΔG are usually written with "rxn" (or "sys") omitted ...

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

It turns out that free energy change is the work than can be done on the surroundings (excluding any pressure volume work), and so tells us how much work we can get from a chemical transformation.

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System-only spontaneity measure

ΔG depends only on system quantities, but it is equivalent to ΔS_{tot}.

If $\Delta G < 0$, then spontaneous ($\Delta S_{\text{tot}} > 0$) and process provides work

If $\Delta G = 0$, then equilibrium ($\Delta S_{\text{tot}} = 0$) and no work is involved

If $\Delta G > 0$, then non-spontaneous ($\Delta S_{\text{tot}} < 0$) and process requires work

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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, ΔU, ΔS_{sys}, and ΔG when 1.00 mol of 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.

$q_p = 38700$ J

$w = -P\Delta V = -\Delta n_g RT = -1 mol RT$

$\Delta n_g = n_f - n_i = 1 mol - 0$

$= -1 mol \times 8.314 J/(mol K) \times (273+78) K$

$= -2920$ J

$\Delta U = q + w = (38700 - 2920)$ J

$= 35800$ J

$Et(l) \rightarrow Et(g)$

$\Delta H_{sys} = \Delta H_{vap} = 38.7$ kJ/mol

$T_{bp} = 78°C$

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

$\Delta S = \frac{\Delta H}{(273+78) K}$

$\Delta G = 38.7 kJ - (273+78) K \times \frac{38.7 kJ}{(273+78) K}$

$= 0$

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Effect of temperature on spontaneity

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

?

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Atomic or molecular oxygen?

$\Delta G = -T\Delta S_{tot}$ //

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

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

How to proceed?

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

$\Delta H = 2\Delta H_f(O,g) - \Delta H_f(O_2,g)$

$= 2 \times 249.2$ kJ $- 0$

$\Delta S = 2S°(O,g) - S°(O_2,g)$

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

$\Delta H - T\Delta S = \Delta G = -T\Delta S_{tot}$

$-T\Delta S_{sys} = \Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$

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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,

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

At what T will decomposition become spontaneous?

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

$T = 2 \cdot 249.2 \times 10^3/(2 \times 161.1 - 205.0) = 4253$ 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 ...

71% 1. endothermic
29% 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 ...

63% 1. decompose into H_2 and O_2
38% 2. will not decompose into H_2 and O_2
0% 3. More information needed

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

19% 1. only at low temperature
38% 2. only at high temperature
6% 3. always
38% 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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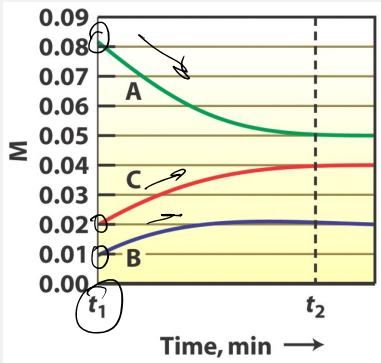
Spontaneous approach to equilibrium: A → B + C



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Reaction quotient Q measures progress

A → B + C

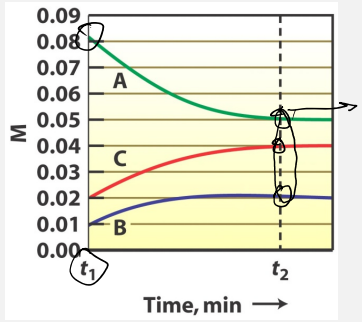
Q = products/reactants = [B][C]/[A]

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 $A \rightarrow B + C$, 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 ...

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

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Practice: Problem 14.5

$K = \frac{(P_{H_2}/\text{atm})(P_{CO_2}/\text{atm})}{(P_{CO}/\text{atm})(P_{H_2O}/\text{atm})}$

$3.9 = \frac{x \; 0.70}{(0.10)(0.10)}$

$x = \frac{3.9 * 0.010}{0.70}$

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

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

0.10 0.10 0.70 x

(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 $H_2(g)$.

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Practice: Problem 14.11

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

(a) $K = \frac{([HCO_3^-]/M)^6}{([As(OH)_6^{3-}]/M)^2 (P_{CO_2}/\text{atm})^6}$

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

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

① No (s) or (l)

② [ ]/M, P/atm

③ stoichiometric coefficients as powers

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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 , $\Delta G < 0$, $\Delta S_{tot} > 0$

$Q = \frac{\text{product}}{\text{reactant}}$

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

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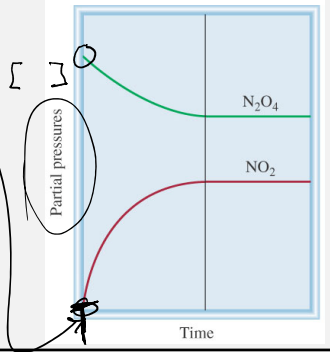
$N_2O_4 \rightleftharpoons 2\ NO_2$

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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$N_2O_4 \rightleftharpoons 2\ NO_2$

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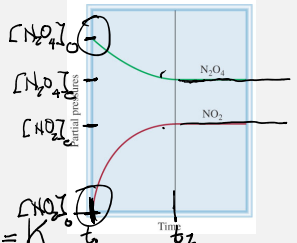
[TP] The figure shows how the partial pressures of the N_2O_4 and NO_2 change with time due to the chemical reaction

$N_2O_4 \rightleftharpoons 2\ NO_2$

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

63% 1. It is spontaneous
6% 2. It is at equilibrium
31% 3. It is non-spontaneous
0% 4. Its spontaneity is not known without further information



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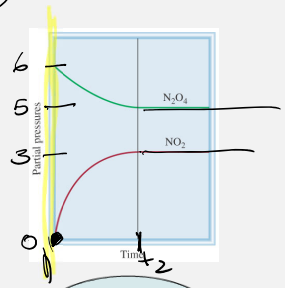
[TP] At the initial conditions for the reaction

$N_2O_4 \rightleftharpoons 2\ NO_2$

the following is known about the ratio Q/K.

18% 1. It is greater than 1
18% 2. It is equal to 1
65% 3. It is less than 1
0% 4. The ratio is not known without further information



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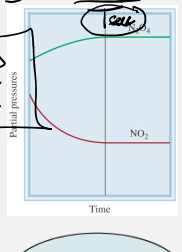
[TP] The figure shows how the partial pressures of the N_2O_4 and NO_2 change with time due to the chemical reaction

$$N_2O_4 \rightleftharpoons 2\ NO_2$$

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

29% 1. It is spontaneous
6% 2. It is at equilibrium
65% 3. It is non-spontaneous
0% 4. Its spontaneity is not known without further information



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