[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 ...

29%	1.	endothermic
0%	2.	exothermic
0%	3.	neither ($\Delta H = 0$)
0%	4.	More information needed
71%	5.	Not sure

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Lecture 13 CH131 Summer 1 2021

Thursday, June 17, 2021

- Effect of temperature on spontaneity

Begin ch14:Chemical equilibrium
- Reaction quotient, spontaneity, and equilibrium
- Q algebra: Q (and so K) depends on how a reaction is written
- Predicting direction of change
- Calculate equilibration using an ICE table

Next: Approximating equilibration; Equilibrium calculation examples; Effect of temperature on equilibrium: $\Delta G = RT\ln(Q/K) = \Delta H - T\Delta S$; Disturbing equilibrium; Begin Ch15: Acid-base equilibria

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Effect of temperature on spontaneity // $\Delta S = \frac{heat}{T}$

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Atomic or molecular oxygen?

$\Delta G > 0$, non-spontaneous

$\Delta G \equiv -T\Delta S_{tot}$.

At SATP, oxygen exists as a diatomic gas.

This means the free energy change for the process $O_2(g) \rightarrow 2\,O(g)$ must be positive and quite large at SATP.

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

$$\Delta H_{rxn} = 2\Delta H_f^\circ(O,g) - \Delta H_f^\circ(O_2,g)$$

$$\Delta H_f^\circ(O_2,g) = 0$$

$$\Delta S_{rxn} = 2S^\circ(O,g) - S^\circ(O_2,g)$$

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Atomic or molecular oxygen?

Indeed, using

$\Delta H°_f(\mathrm{O}, g) = 249.2$ kJ/mol

$S°(\mathrm{O}, g) = 161.1$ J/(K mol)

$S°(\mathrm{O_2}, g) = 205.0$ J/(K mol)

the free energy change for $\mathrm{O_2}(g) \rightarrow 2\,\mathrm{O}(g)$ is

$$\Delta G°/\frac{\mathrm{kJ}}{\mathrm{mol}} = 2 \times 249.2 - 298\ \mathrm{K} \times 10^{-3}(2 \times 161.1 - 205.0) = +463$$

W_e O_2

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Atomic or molecular oxygen?

$$\Delta G°/\frac{\mathrm{kJ}}{\mathrm{mol}} = 2 \times 249.2 - 298\ \mathrm{K} \times 10^{-3}(2 \times 161.1 - 205.0) = +463$$

The reason $\Delta G°$ is so large and positive is ~~large~~ entropy decrease in the surroundings, necessitated by the 2 × 249.2 kJ/mol of heat needed by the system to break the bonds between the pairs of oxygen atoms.

The entropy increase in the system, due to the doubling of gaseous particles, is not large enough to offset the large entropy decrease in the surroundings.

$O_2 \rightarrow 2O$ $\quad \Delta S_{sys} > 0$

W_p $\quad \Delta S_{sur} \ll 0$

$\Delta S_{tot} < 0$

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Atomic or molecular oxygen?

$$\Delta G°/\frac{\mathrm{kJ}}{\mathrm{mol}} = 2 \times 249.2 - 298\ \mathrm{K} \times 10^{-3}(2 \times 161.1 - 205.0) = +463$$

But what about increasing the temperature to mute the effect of heat withdrawn from the surroundings, since $\Delta S_{sur} = -\Delta H_{sys}/T$?

This would enhance the contribution of the system entropy increase, ΔS_{sys}.

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Atomic or molecular oxygen?

Above what T will the decomposition $\mathrm{O_2}(g) \rightarrow 2\,\mathrm{O}(g)$ become spontaneous?

The decomposition will be spontaneous above the temperature at which

$$\Delta G/\frac{\mathrm{kJ}}{\mathrm{mol}} = 0 = 2 \times \overset{\Delta H_{f}}{249.2} - \frac{T}{\mathrm{K}} \times 10^{-3}\overbrace{(2 \times 161.1 - 205.0)}^{\Delta S_{sys}}$$

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

So, for T above 4253 K, O atoms will predominate.

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Atomic or molecular oxygen?

The more T exceeds 4253 K, the greater the relative amount of O atoms to O_2 molecules.

We'll soon learn how to quantify the relative amounts for each temperature.

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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
0% 5. Not sure

$\Delta S_{surr} = \frac{heat_{surr}}{T}$

$\to \Delta S_{rxn} = +130\ J/K$

$\Delta S_{surr} < 0$

$\Rightarrow \Delta S_{tot} < 0$

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

0% 1. only at low temperature
0% 2. only at high temperature
0% 3. always
100% 4. never
0% 5. Further information required
0% 6. Not sure

$\Delta H_{rxn} > 0 \Rightarrow \Delta S_{surr} < 0$

$\Delta S_{sys} < 0$

$\Delta S_{tot} = \underbrace{\Delta S_{surr}}_{\text{"}<0\text{"}} + \underbrace{\Delta S_{sys}}_{\text{"}<0\text{"}}$

$= \frac{\Delta H_{surr}}{T} + \Delta S_{sys}$

$\Delta H_{surr} = -\Delta H_{sys}$ < 0

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Begin ch14: Chemical equilibrium

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Spontaneity of “reactants” → “products”

We have learned how to calculate chemical amounts using ICF (Initial, Change, Final) tables considering the limiting reagent and the percent yield.

The yield is not always 100% because the spontaneity depends on the amount of reactants and products present.

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Spontaneity of “reactants” → “products”

Chemical reactions proceed until the forward and reverse reactions exactly balance one another.

That is, until the reactants and products are in equilibrium.

That is, until $\Delta G = 0$.

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Spontaneity of “reactants” → “products”

If products (right side) increase with time, we say the reaction is spontaneous, $\Delta G < 0$.

If reactants (left side) increase with time, we say the reaction is nonspontaneous, $\Delta G > 0$.

If the amount of reactants and products do not change with time, we say the reaction is at equilibrium, $\Delta G = 0$.

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Reaction quotient Q measures reaction progress

For $a\text{A} \to b\text{B} + c\text{C}$, the reaction quotient is a specific measure of the ratio of the amount of products present to the amount of reactants present,

$$Q = \frac{[\text{B}]^b[\text{C}]^c}{[\text{A}]^a} = \frac{\text{product}}{\text{reactant}} = \text{a number (no units)}$$

The amounts [A], etc., are the numerical values of molarity (mol/L) for solutes and the numerical value of the partial pressure (in atm) .

Because units are omitted, the reaction quotient is a number without units.

omit any solids or liquid.

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Reaction quotient Q measures reaction progress

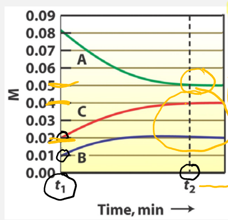
If the system is not at equilibrium, as time passes the value of Q changes as the chemical transformation proceeds.

Once equilibrium is established, Q will not longer change and its value is called the equilibrium constant,

$$Q \text{ at eqilibrium} = K = \frac{[\mathrm{B}]_e^b\,[\mathrm{C}]_e^c}{[\mathrm{A}]_e^a}$$

At time t_1 $[B]=0.01$, $[C]=0.02$, $[A]=0.08$

$$Q(t_1) = \frac{(0.01)(0.02)^3}{(0.08)^2} = 0.0000125$$



$[A]=0.05$, $[C]=0.04$, $[B]=0.02$

$$Q(t_2) = \frac{(0.02)(0.04)^3}{(0.06)^2} = 4.10 = 0.000356$$

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Practice: Problem 14.5

$K = Q$ when at equilibrium

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

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 $H_2(g)$.

$$P_{H_2} = 3.9\,P_{CO}P_{H_2O}/P_{CO_2}$$

$$= \frac{3.9 * 0.10 * 0.10}{0.70} = \frac{0.039}{0.70} = \underline{0.056}\ //$$

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

$$K_a = \frac{[Zn^{2+}]_e}{[Ag^+]_e^2}$$

$$K_b = \frac{[HCO_3^-]_e^6}{[As(OH)_6^{3-}]_e^2\,P_{CO_2,e}^6}$$

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The value of Q (and so K) depends on how a chemical reaction is written.

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Q depends on how a reaction is written

At a certain time, the value of the reaction quotient for the reaction

$2\,A + B \rightleftharpoons 2\,C$

is $Q_1 = 4.0$. $= \dfrac{[C]^2}{[A]^2[B]}$

At the same time, what would be the value of Q be for the reaction

$4\,A + 2\,B \rightleftharpoons 4\,C$?

$Q_4 = (C)^4/((A)^4(B)^2) = (Q_1)^2 = 16$

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Q depends on how a reaction is written

At a certain time, the value of the reaction quotient for the reaction

$2\,A + B \rightleftharpoons 2\,C$ $\dfrac{[C]^2}{[A]^2[B]} = 4.0$

is $Q_1 = 4.0$.

At the same time, what would be the value of Q be for the reaction

$2\,C \rightleftharpoons 2\,A + B$? $[A]^2[B]$

$Q_2 = (A)^2(B)/(C)^2 = 1/Q_1 = 0.25$ $\dfrac{1}{\dfrac{[C]^2}{[A]^2[B]}} = \dfrac{1}{4.0} = 0.25$

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Q depends on how a reaction is written

At a certain time, here are the values of the reaction quotients for two different reactions,

$2\,A \rightleftharpoons B,\ \ Q_5 = (B)/(A)^2 = 2$ $= \dfrac{[B]}{[A]^2}$

$C \rightleftharpoons 3\,D,\ \ Q_6 = (D)^3/(C) = 5$ $\dfrac{[D]^3}{[C]}$

At the same time, what would be the value of Q be for the reaction

$2\,A + C \rightleftharpoons B + 3D$?

$Q_7 = (B)(D)^3/((A)^2(C)) = Q_5 \times Q_6 = 10$

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[TP] The value of the equilibrium constant for the reaction

$2\,A \rightleftharpoons C$ is $K_1 = 4$

and that for the reaction

$D \rightleftharpoons C$ is $K_2 = 0.5$.

The value of the equilibrium constant for the reaction

$2\,A \rightleftharpoons D$ is $K_3 = \ldots$

10%	1.	2
0%	2.	4
0%	3.	6
90%	4.	8
0%	5.	None of the above
0%	6.	Not sure

$2A \rightleftharpoons \cancel{C}$ $K_1 = 4$

$\cancel{C} \rightleftharpoons D$ $1/K_2 = 2$

$2A \rightleftharpoons D$ $4 * 2 = 8$

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Predicting direction of change

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[TP] For the reaction 2 A + B → 2 C, at a certain time the value of its reaction quotient is $Q = 7$. This means the value of the equilibrium constant for the reaction is ...

0%	1.	< 7 — Too much product.
0%	2.	7 — No change, be at equil.
50%	3.	> 7 — Too much reactant
0%	4.	Further information needed
50%	5.	Not sure

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[TP] The value of the equilibrium constant for the gas-phase reaction

2 A + B → C is $K = 10$.

At a certain time, the partial pressures are A, B and C are, respectively, 1 bar, 1 bar and 2 bar. The value of the reaction quotient is $Q =$ ...

$$Q = \frac{P_C}{P_A^2 P_B} = \frac{2}{1 * 1} = 2$$

100%	1.	2
0%	2.	10
0%	3.	Further information needed
0%	4.	Not sure

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[TP] The value of the equilibrium constant for the gas-phase reaction

2 A + B → C is $K = 10$.

At a certain time, the partial pressures are A, B and C are, respectively, 0.2 bar, 1 bar and 4 bar. The value of the reaction quotient is $Q =$ ...

$$\frac{P_C}{P_A^2 P_B} = \frac{4}{(0.2)^2\, 1} = \frac{4}{0.04} = 100$$

0%	1.	0.04
0%	2.	4
0%	3.	10
90%	4.	100
0%	5.	None of the these
10%	6.	Not sure

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[TP] The value of the equilibrium constant for the gas-phase reaction
$2\,A + B \rightarrow C$ is $K = 10$.
At a certain time, the partial pressures are A, B and C are such that the value of the reaction quotient is $Q = 100$. As time passes, the value of Q will ...

10% 1. increase
0% 2. stay the same
90% 3. Decrease
0% 4. Not sure

$Q = \frac{\text{products}}{\text{reactants}} = 100$ } Too much product, Too little reactant

$K = 10$

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[TP] The value of the equilibrium constant for the gas-phase reaction
$2\,A + B \rightarrow C$ is $K = 10$.
At a certain time, the partial pressures are A, B and C are such that the value of the reaction quotient is $Q = 6$. As time passes, the value of Q will ...

100% 1. increase
0% 2. stay the same
0% 3. Decrease
0% 4. Not sure

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Calculate equilibration using an ICE table

When the equilibrium constant is neither very big or very small, the calculation of equilibrium amounts must be done exactly.

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Calculate equilibration using an ICE table

$A(g) \leftrightharpoons B(g) + C(g) \quad K = 5.0$

	A(g)/atm	B(g)/atm	C(g)/atm
Initial	3.0	2.0	1.0
Change	$-x$	$+x$	$+x$
Equilibrium	$3.0-x$	$2.0+x$	$1.0+x$

$K = 5.0 = \frac{(2.0+x)(1.0+x)}{(3.0-x)}$

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Calculate equilibration using an ICE table

$A(g) \leftrightharpoons B(g) + C(g) \quad K = 5.0,\ Q = 0.67$, too little product

	$A(g)/M$	$B(g)/M$	$C(g)/M$
Initial	3.0	2.0	1.0
Change	$-x$	$+x$	$+x$
Equilibrium			

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Calculate equilibration using an ICE table

$A(g) \leftrightharpoons B(g) + C(g) \quad K = 5.0\text{ M},\ Q = K$, equilibrium

	$A(g)/M$	$B(g)/M$	$C(g)/M$
Initial	3.0	2.0	1.0
Change	$-x$	$+x$	$+x$
Equilibrium	$3.0 - x$	$2.0 + x$	$1.0 + x$

$$K = \frac{[B][C]}{[A]} = \frac{(2.0+x)(1.0+x)}{(3.0-x)}$$

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Calculate equilibration using an ICE table

$A(g) \leftrightharpoons B(g) + C(g) \quad K = 5.0,\ Q = K$, equilibrium

	$A(g)/M$	$B(g)/M$	$C(g)/M$
Initial	3.0	2.0	1.0
Change	$-x$	$+x$	$+x$
Equilibrium	1.6	3.4	2.4

$$K = \frac{[B][C]}{[A]} = \frac{(2.0+x)(1.0+x)}{(3.0-x)} \rightarrow x = 1.4$$

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$2A + B \rightarrow 3C \quad Q = 8,\ K = 2$

	$2A$	B	$3C$
I	1	1	2
C	$+2x$	$+x$	$-3x$
E	$(1+2x)$	$1+x$	$2-3x$

$$K = 2 = \frac{P_C^3}{P_A^2\, P_B} = \frac{(2-3x)^3}{(1+2x)^2(1+x)} \rightarrow \text{cubic equation}$$

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