

Problems sheet for the 3rd exam (December 15, 2018)

Physical Chemistry for Energy Engineering

*1: Please do not write answers in this problems sheet. What is written in the problems sheet is not evaluated.

*2: Please return both the problems sheet and the answer sheet after the exam.

[Problem-I: 35 pt]

(1) Fill the blank (a), (b) and (c). [6pt]

For a typical chemical reaction described with " $\nu_A A + \nu_B B \rightarrow \nu_Y Y + \nu_Z Z$ ", the rate of reaction, $v(t)$, is written as

$v(t) = \boxed{(a)}$. Then, the relationship between $v(t)$ and the concentrations of the reactants and the products is called the rate

law. $\boxed{(b)}$ is an abstract one-dimensional coordinate which represents progress along a reaction pathway. It usually

represents a set of geometrical parameters (bond length, bond angle, etc) that change during the reaction. If a reaction is

simple, it is represented by a sole quantity: for example, $\boxed{(b)}$ for the atomization reaction of a diatomic molecule is usually

$\boxed{(c)}$.

$$(a) v(t) = -\frac{1}{\nu_A} \frac{d[A]}{dt} = -\frac{1}{\nu_B} \frac{d[B]}{dt} = \frac{1}{\nu_Y} \frac{d[Y]}{dt} = \frac{1}{\nu_Z} \frac{d[Z]}{dt} = \frac{1}{V} \frac{d\xi}{dt}$$

(b) Reaction coordinate(s)

(c) interatomic-distance

(2) There may be some wrong description in the following sentences. First, please judge if the sentence is correct or not. Then, if not correct, please point out what is wrong and modify it. [6pt]

(a) If there is a reversible reaction, like $A \rightleftharpoons B$, there is a general relationship between rate constants (k_1 for forward reaction and k_{-1} for backward reaction) and rate constants (K_C), namely $K_C = k_1/k_{-1}$. It is called the "principle of detailed balance".

Incorrect: This is true only when forward and backward reactions are elementary, not complex.

(b) The meaning of "reversible" is different between thermodynamics (like reversible process) and chemical kinetics (like reversible reaction). For chemical kinetics, when we say "the reaction is reversible", we consider that the rate of backward reaction is comparable with the rate of forward reaction and thus should be taken into account. Note that any chemical reaction basically holds the forward and the backward reactions. If the backward reaction is negligibly slow and less-frequent in comparison with the forward reaction, the reaction is not considered "reversible" in practice.

Correct

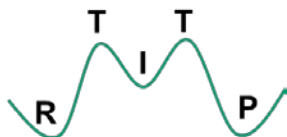
(c) The length of time required for half of the reactant to disappear is called the half-life of the reaction and is written as $t_{1/2}$. The half-life of the first-order reaction does not depend on the initial concentration. Hence, the time required to reduce the amount to half is constant, independent of the concentration. Because radioactive decays are first-order reactions, the half-life of radioactive nuclide also holds the same features in general.

Correct

(d) The rate laws often have the form " $v(t) = k[A]^{m_A}[B]^{m_B} \dots$ ", where $[A]$, $[B]$, ... are the concentrations of the various reactants and k is the rate constant and the exponents or orders, m_A , m_B , ... are constants. Except for some special cases, the orders are usually equal to the stoichiometric coefficients: for example, $v(t) = k[A]^{\nu_A}[B]^{\nu_B}$ for " $\nu_A A + \nu_B B \rightarrow \nu_Y Y + \nu_Z Z$ ".

Incorrect: This is not usual. Many reactions do not follow that form and most reactions do not satisfy $m_A = \nu_A$.

(3) Explain the difference between (a) activated complex, (b) reaction intermediate, and (c) transition state. [5pt]



This figure explains the difference/similarity between them. 'R' indicates the reactants, which is the initial state of the reaction. 'P' indicates the products, which is the final state of the reaction. In this reaction, we have another (locally) stable state, which is reaction intermediate denoted with 'I'. The transition state is the state the highest barrier state between R and I, R and P, or I and P, which is denoted as 'T' in the figure. "Activated complex" is the same with the

transition state. (Strictly speaking, “transition state” more focus on ‘state’, so it is usually used with “initial state” or/and “final state”. “Activated complex” more focus on the chemical compound itself, so it is usually used with “reactants” or/and “products”.)

(4) Explain the difference between (a) complex reaction and (b) elementary reaction. [4pt]

For a complex reaction, there are one or multiple reaction intermediate(s). On the other hand, for an elementary reaction, there is no reaction intermediate. So, the difference is whether reaction intermediate(s) (a) exist or (b) not.

(5) The temperature dependence of the rate constant is usually expressed by Arrhenius equation, namely

$$k = A \exp\left(-\frac{E}{RT}\right). \text{ Explain what kind of physics and chemistry are reflected in the parameters A and E. [6pt]}$$

In the transition state theory with “A + B → P” with ideal gasses, the rate constant is expressed as

$$k(T) = \frac{k_B T}{h c^\circ} e^{-\Delta^\ddagger G^\circ / RT} = \frac{e^2 k_B T}{h c^\circ} e^{\Delta^\ddagger S^\circ / R} e^{-E_a / RT}$$

where $E_a = \Delta^\ddagger H^\circ + 2RT$ and $\Delta^\ddagger G^\circ$ (and similarly $\Delta^\ddagger S^\circ$ and $\Delta^\ddagger H^\circ$) are the change in Gibbs energy (entropy and enthalpy) in going from the reactants at a concentration c° to the transition state at a concentration c° . In

comparison with the Arrhenius equation, $A = \frac{e^2 k_B T}{h c^\circ} e^{\Delta^\ddagger S^\circ / R}$ and $E = E_a = \Delta^\ddagger H^\circ + 2RT$. Thus, A is related to the entropy difference, such as the disorderness of the relative structures between the activated complex and the reactants and the reaction trial frequency between the activated complex and the reactants, while E is related to the energy (mostly potential energy) difference between the activated complex and the reactants.

(6) For an elementary reaction $A \rightleftharpoons B$, if exists, derive a general relationship between k_1 , k_{-1} and K_C . K_C is the equilibrium constant regarding the concentration (not partial pressure). k_1 and k_{-1} are the rate constants for the forward and the backward reactions. [4pt]

According to the assumption of the elementary reaction, the rate laws are written as

$$v_1 = -\frac{d[A]}{dt} = k_1[A] \quad \text{and} \quad v_{-1} = -\frac{d[B]}{dt} = k_{-1}[B]$$

At equilibrium state, $K_C = [B]_{eq} / [A]_{eq}$ and $v_1 = v_{-1}$ thus $k_1[A]_{eq} = k_{-1}[B]_{eq}$.

Hence, $K_C = k_1 / k_{-1}$.

(7) For a general complex reaction $A \rightleftharpoons B$, if exists, derive a general relationship between k_1 , k_{-1} and K_C . Explain why the result is different from (or similar to) the result of (6). [4pt]

In a general complex reaction, the rate laws of the forward and backward reactions cannot be simply written as

$$v_1 = -\frac{d[A]}{dt} = k_1[A] \quad \text{and} \quad v_{-1} = -\frac{d[B]}{dt} = k_{-1}[B]$$

Therefore, $K_C = [B]_{eq} / [A]_{eq}$ cannot be simply and generally expressed as in (6).

[Problem-II: 10 pt → 11pt]

For a general chemical equilibrium equation for ideal gasses like

“ $\nu_A A(g) + \nu_B B(g) \rightleftharpoons \nu_Y Y(g) + \nu_Z Z(g)$ ”, the equilibrium constant $K_p(T)$ at a constant-pressure constant-temperature condition is described as

$$K_p(T) = \left[\frac{(P_Y/P^\circ)^{\nu_Y} (P_Z/P^\circ)^{\nu_Z}}{(P_A/P^\circ)^{\nu_A} (P_B/P^\circ)^{\nu_B}} \right]_{eq} = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right)$$

where $\Delta_r G^\circ = \nu_Y \mu_Y^\circ(T) + \nu_Z \mu_Z^\circ(T) - \nu_A \mu_A^\circ(T) - \nu_B \mu_B^\circ(T)$, P° is the standard pressure (1 bar), and P_A , P_B , P_Y and P_Z are the partial pressures of gasses A(g), B(g), Y(g) and Z(g), respectively. Note that “constant-pressure” is about the total pressure, not about the partial pressure.

Please derive the equation “ $K_p(T) = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right)$ ” starting from the condition of thermodynamical equilibrium state at a constant-pressure constant-temperature condition.

The amount of species i is n_i [mol]. The Gibbs energy for this multi-component system is a function of T, P, n_A, n_B, n_Y and n_Z , then the total differential is:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_A, n_B, n_Y, n_Z} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_A, n_B, n_Y, n_Z} dP + \left(\frac{\partial G}{\partial n_A}\right)_{T, P, n_B, n_Y, n_Z} dn_A + \left(\frac{\partial G}{\partial n_B}\right)_{T, P, n_A, n_Y, n_Z} dn_B + \left(\frac{\partial G}{\partial n_Y}\right)_{T, P, n_A, n_B, n_Z} dn_Y + \left(\frac{\partial G}{\partial n_Z}\right)_{T, P, n_A, n_B, n_Y} dn_Z$$

Then, it can be re-written as:

$$dG = -SdT + VdP + \mu_A dn_A + \mu_B dn_B + \mu_Y dn_Y + \mu_Z dn_Z$$

$$\mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{T, P, n_B, n_Y, n_Z}, \text{ etc}$$

If the reaction takes place in const.-T const.-P condition,

$$dG = \mu_A dn_A + \mu_B dn_B + \mu_Y dn_Y + \mu_Z dn_Z \quad (\text{constant T and P})$$

*This "const.-P" is about total pressure (not partial pressure).

We define a quantity ξ , called as the "extent of reaction". Here n_{i0} is the initial number of moles for species i , then :

$$n_A = n_{A0} - \nu_A \xi \quad n_B = n_{B0} - \nu_B \xi \quad (\text{reactants})$$

$$n_Y = n_{Y0} + \nu_Y \xi \quad n_Z = n_{Z0} + \nu_Z \xi \quad (\text{products})$$

In this case, ξ has units of moles. Then, the variations of n_i is:

$$dn_A = -\nu_A d\xi \quad dn_B = -\nu_B d\xi \quad (\text{reactants})$$

$$dn_Y = \nu_Y d\xi \quad dn_Z = \nu_Z d\xi \quad (\text{products})$$

*Note that the unit for $d\xi$ is [mol].

which means that as the reaction (left to right) proceeds, the reactants decrease and the products increase according to the stoichiometry.

Using these equations:

$$dG = \mu_A dn_A + \mu_B dn_B + \mu_Y dn_Y + \mu_Z dn_Z = (-\nu_A \mu_A - \nu_B \mu_B + \nu_Y \mu_Y + \nu_Z \mu_Z) d\xi \quad (\text{constant T and P})$$

$$dG = (-\nu_A \mu_A - \nu_B \mu_B + \nu_Y \mu_Y + \nu_Z \mu_Z) d\xi \quad (\text{constant T and P})$$

$$\left(\frac{\partial G}{\partial \xi}\right)_{T, P} = \nu_Y \mu_Y + \nu_Z \mu_Z - \nu_A \mu_A - \nu_B \mu_B$$

Here, we define $\left(\frac{\partial G}{\partial \xi}\right)_{T, P} = \Delta_r G$, which is the change in Gibbs energy when the extent of reaction changes by one mole, and its unit is [J mol⁻¹].

Assuming each species behaves as ideal gas, as the pressure dependence of chemical potential is written as $\mu_j(T, P) = \mu_j^\circ(T) + RT \ln(P_j/P^\circ)$, then:

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$

$$Q = \frac{(P_Y/P^\circ)^{\nu_Y} (P_Z/P^\circ)^{\nu_Z}}{(P_A/P^\circ)^{\nu_A} (P_B/P^\circ)^{\nu_B}}$$

P° is the pressure of standard state (1 bar) and P_A is the partial pressure of species A.

$$\Delta_r G^\circ = \nu_Y \mu_Y^\circ(T) + \nu_Z \mu_Z^\circ(T) - \nu_A \mu_A^\circ(T) - \nu_B \mu_B^\circ(T)$$

Here, the quantity $\Delta_r G^\circ$ is the change in standard Gibbs energy for the reaction between **unmixed reactants** to form **unmixed products**. All species in their standard states at T and P° . Note that $P^\circ = 1$ bar.

When the reaction system is equilibrium, the Gibbs energy must be the minimum with respect to any change from the equilibrium state, thus

$$\left(\frac{\partial G}{\partial \xi}\right)_{T, P} = \Delta_r G = \Delta_r G^\circ + RT \ln Q_{eq} = 0 \text{ at an equilibrium state. Thus:}$$

$$\Delta_r G^\circ = -RT \ln \left(\frac{P_Y^{\nu_Y} P_Z^{\nu_Z}}{P_A^{\nu_A} P_B^{\nu_B}} \right)_{eq} = -RT \ln K_p(T)$$

Finally, we confirm the temperature and pressure dependence of the chemical potential of an ideal gas.

$$\mu_j(T, P) = \mu_j^\circ(T) + RT \ln(P_j/P^\circ)$$

For an ideal gas:

$$PV = nRT$$

$$U = nC_V T + \text{constant} = nC_V T + nU_0 \quad \text{then } dU = nC_V dT$$

For a path keeping some thermal equilibrium states (i.e. reversible process):

$$dU = TdS - PdV$$

$$dS = \frac{dU}{T} + \frac{PdV}{T} = nC_V \frac{dT}{T} + nR \frac{dV}{V}$$

$$S(T, V) = \int nC_V \frac{dT}{T} + \int nR \frac{dV}{V} = nS_0 + nC_V \ln T + nR \ln V$$

$$G(T, V) = U + PV - TS = nC_V T + nU_0 + nRT - T\{nS_0 + nC_V \ln T + nR \ln V\}$$

$$G(T, P) - G(T, P_0) = -T\{nR \ln V\} + T\{nR \ln V_0\} = T_1 \left\{ nR \ln \frac{V_0}{V} \right\}$$

$$P_1 V_1 = P_2 V_2$$

$$G(T, P) - G(T, P_0) = T_1 \left\{ nR \ln \frac{V_0}{V} \right\} = T_1 \left\{ nR \ln \frac{P}{P_0} \right\}$$

$$\mu = \left(\frac{\partial G}{\partial n} \right)_{P, T}$$

$$\mu(T, P) = \mu(T, P^\circ) + RT \ln \frac{P}{P^\circ} = \mu^\circ(T) + RT \ln \frac{P}{P^\circ}$$

Here $P^\circ = 1 \text{ bar}$ for the standard chemical potential.

[Problem-III: 16 pt→18pt]

(1) Calculate $\Delta_r G^\circ$ and K_p of the following reaction: $\text{NH}_3(\text{g}) \rightleftharpoons \frac{3}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{N}_2(\text{g})$. Please assume that the standard molar Gibbs energy of formation for NH_3 is -16.367 kJ/mol at 298.15 K and 1 bar . **(4pt)**

$$\begin{aligned}\Delta_r G^\circ &= \sum_i^{\text{products}} \nu_i \mu_i^\circ - \sum_j^{\text{reactants}} \nu_j \mu_j^\circ = \frac{3}{2} \mu_{\text{H}_2}^\circ(T) + \frac{1}{2} \mu_{\text{N}_2}^\circ(T) - \mu_{\text{NH}_3}^\circ(T) \\ &= \frac{3}{2} \Delta_f G^\circ_{\text{H}_2}(T) + \frac{1}{2} \Delta_f G^\circ_{\text{N}_2}(T) - \Delta_f G^\circ_{\text{NH}_3}(T) = (0) + (0) - (-16.367) = 16.367 \text{ kJ/mol} \\ K_p(T) &= \exp\left(-\frac{\Delta_r G^\circ}{RT}\right) = \exp\left(-\frac{16.367 \times 10^3}{8.31 \times 298.15}\right) = 0.001352 = 1.352 \times 10^{-3}.\end{aligned}$$

(2) If the initial amount of gasses are "1 mol for NH_3 and 0 mol for H_2 and N_2 ", determine the equilibrium partial pressures of NH_3 , H_2 and N_2 , if the temperature is 298.15 K and the total pressure is 1 bar . **(6pt)**

Using the extent of reaction with ξ , the amounts as a function of the extent of reaction are given as

$P_{\text{NH}_3} = (1 - \xi) \text{ mol}$, $P_{\text{H}_2} = 1.5\xi \text{ mol}$ and $P_{\text{N}_2} = 0.5\xi \text{ mol}$, where the total gas amount is given as $(1 + \xi) \text{ mol}$. As total pressure is fixed at 1 bar , partial pressures are expressed as

$$P_{\text{NH}_3} = \frac{(1-\xi)}{1+\xi} \text{ bar}, P_{\text{H}_2} = \frac{1.5\xi}{1+\xi} \text{ bar} \text{ and } P_{\text{N}_2} = \frac{0.5\xi}{1+\xi} \text{ bar}$$

At the equilibrium state, ξ (specifically, ξ_{eq}) must satisfy the following equation:

$$\begin{aligned}K_p(T) &= \left[\frac{(P_{\text{H}_2}/P^\circ)^{1.5} (P_{\text{N}_2}/P^\circ)^{0.5}}{(P_{\text{NH}_3}/P^\circ)^1} \right]_{eq} = \frac{\left(\frac{1.5\xi_{eq}}{1+\xi_{eq}}\right)^{1.5} \left(\frac{0.5\xi_{eq}}{1+\xi_{eq}}\right)^{0.5}}{\left(\frac{1-\xi_{eq}}{1+\xi_{eq}}\right)} = \frac{(1.5^{1.5} \times 0.5^{0.5})(\xi_{eq})^2}{(1-\xi_{eq})} \frac{1}{1+\xi_{eq}} = \frac{1.299(\xi_{eq})^2}{(1-\xi_{eq}^2)} = 1.352 \times 10^{-3} \\ 1.299(\xi_{eq})^2 &= 1.352 \times 10^{-3}(1 - \xi_{eq}^2)\end{aligned}$$

As $\xi_{eq} > 0$ is needed, $\xi_{eq} = 0.0322$ is achieved. Thus, the partial pressures are

0.938 bar for NH_3 , 0.0469 bar for H_2 and 0.0156 bar for N_2 .

(3) From the equilibrium state achieved in (2), does NH_3 increase by increasing temperature? Answer with scientific reasons. **(4pt)**

$\Delta_r G^\circ$ can be decomposed into $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$. The second term is more dependent on the temperature than the first term. Regarding $\Delta_r S^\circ$, as the products are composed of 2 gas molecules while the reactant is composed of 1 gas molecule, $\Delta_r S^\circ > 0$ is achieved. Thus, $\Delta_r G^\circ$ should decrease as the temperature increases.

If we assume that the temperature dependence of $\Delta_r G^\circ$ is negligibly small, by increasing the temperature, K_p increases. For example, at 500 K , $K_p(500\text{K})_{approximation} = 0.0195$ is achieved, which is larger than $K_p(298.15\text{K}) = 0.001352$.

On the top of this, $\Delta_r G^\circ$ decreases as the temperature increases. As a result, K_p is more increased than our estimate above, namely $K_p(500\text{K})_{true} > K_p(500\text{K})_{approximation} = 0.0195$, for example.

Therefore, we can conclude that the amount (proportional to the partial pressure) of NH_3 decreases.

(4) From the equilibrium state achieved in (2), does NH_3 increase by increasing the total pressure? Answer with scientific reasons. **(4pt)**

As the definition of K_p is given as $K_p(T) = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right)$, where $\Delta_r G^\circ$ is of the standard pressure (usually 1 bar), K_p

is independent of the total pressure. For example, we consider the initial pressure of NH_3 is 2 bar and those of H_2 and N_2 are 0 bar . In this case, with the extent of reaction, the partial pressures are expressed as

$$P_{NH_3} = 2 \frac{(1-\xi)}{1+\xi} \text{ bar}, P_{H_2} = 2 \frac{1.5\xi}{1+\xi} \text{ bar} \text{ and } P_{N_2} = 2 \frac{0.5\xi}{1+\xi} \text{ bar}$$

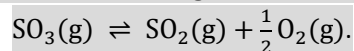
$$\text{Then, } K_p(T) = \left[\frac{(P_{H_2}/P^\circ)^{1.5} (P_{N_2}/P^\circ)^{0.5}}{(P_{NH_3}/P^\circ)^1} \right]_{eq} = 2 \frac{2.544(\xi_{eq})^2}{(1-\xi_{eq})^2} = 1.352 \times 10^{-3}. \text{ Solving this we achieve } \xi_{eq} = 0.016.$$

With respect to the amount, the 1 bar case is [NH₃]:[H₂]:[N₂]=0.955mol: 0.034mol:0.011mol, while the 2 bar case is [NH₃]:[H₂]:[N₂]=0.968mol: 0.024mol:0.008mol. Thus, NH₃ increases by increasing the total pressure.

This result can be explained as follows. Basically, if the initial amount of NH₃ is fixed (e.g. 1mol in these problems), the pressure increases is equivalent with the decrease of the experimental system volume to be used in this chemical process. In the forward reaction, the total amount of gas molecules increase as the reaction proceeds. Then, if the experimental system volume is decreased, the forward reaction is prevented. Thus, the increase of total pressure causes the decrease of the extent of the reaction, which is equivalent with the increase of NH₃.

[Problem-IV: 10 pt] (4pt for $\Delta_r G^\circ$; 3pt for $\Delta_r H^\circ$; 3pt for $\Delta_r S^\circ$)

The experimental data given in the table below were determined for the reaction described by



Approximately calculate $\Delta_r G^\circ$, $\Delta_r H^\circ$, $\Delta_r S^\circ$ at 900 K. You can assume that the molar enthalpy of formation of each molecule does not largely dependent on temperature in this temperature range.

| T [K] | 800 | 825 | 900 | 953 | 1000 |
|-------------------|--------|--------|--------|--------|--------|
| ln K _p | -3.263 | -3.007 | -1.899 | -1.173 | -0.591 |

For gas species, we can write $K_p(T) = \exp\left(-\frac{\Delta_r G^\circ}{RT}\right)$. Thus,

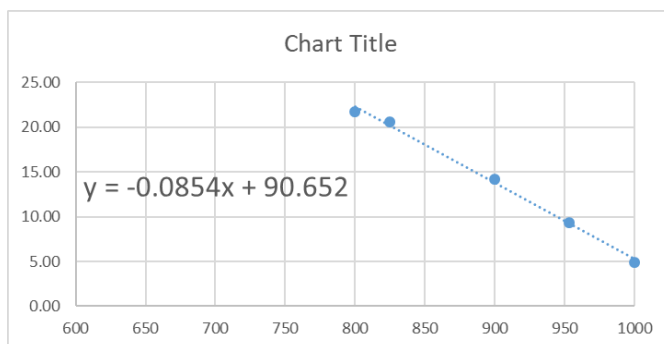
$$-\frac{\Delta_r G^\circ}{RT} = \ln K_p, \text{ then, } \Delta_r G^\circ = -RT \ln K_p$$

Then, we determine $\Delta_r G^\circ$ of given temperature as follows

| T [K] | 800 | 825 | 900 | 953 | 1000 |
|-----------------------------|-------|-------|-------|------|------|
| $\Delta_r G^\circ$ [kJ/mol] | 21.69 | 20.62 | 14.20 | 9.29 | 4.91 |

Assuming the given data is of the constant pressure case, we can write $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$.

Then, by plotting $\Delta_r G^\circ$ as a function of temperature (figure below), we can determine $\Delta_r H^\circ$ and $\Delta_r S^\circ$ from the y-intercept and the slope, respectively. The y-intercept 90.65 [kJ/mol] is equal to $\Delta_r H^\circ$. The slope -0.0854 [kJ/mol/K] is equal to $-\Delta_r S^\circ$. Thus, $\Delta_r S = 85.4$ [J/mol/K].



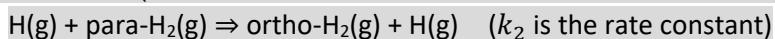
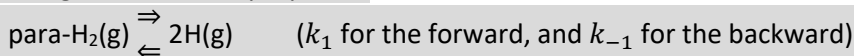
[Problem-V: 12 pt; 8pt for (1) and 4pt for (2)]

(1) The experimentally-observed rate law for the reaction of para-hydrogen to ortho-hydrogen



is $d[\text{ortho-H}_2]/dt = k_{obs}[\text{para-H}_2]^{3/2}$

The following mechanism is proposed:



Please consider that “para-H₂(g) ⇌ 2H(g)” achieves the equilibrium fast, thus the fast-equilibrium approximation is applicable. Then, express k_{obs} in terms of the rate constants for the individual steps of the reaction mechanism.

The rate law of the 2nd reaction is: $v = d[\text{ortho-H}_2]/dt = k_2[\text{H}][\text{para-H}_2]$.

The equilibrium constant is defined as $K_c = \frac{[\text{H}]^2}{[\text{para-H}_2]}$.

Because $v_1 (= k_1[\text{para-H}_2]) = v_{-1} (= k_{-1}[\text{H}]^2)$ is achieved at equilibrium, $K_c = k_1/k_{-1}$ is obtained.

Applying this equation and the first equilibrium approximation, namely $K_c = \frac{[\text{H}]^2}{[\text{para-H}_2]}$, to the rate law,

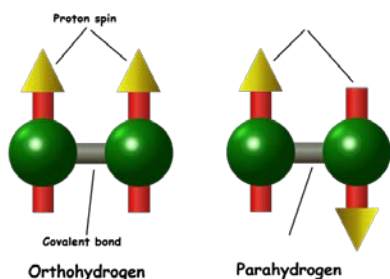
$$d[\text{ortho-H}_2]/dt = k_2[\text{H}][\text{para-H}_2] = k_2\sqrt{K_c}[\text{para-H}_2]^{3/2} = k_2\sqrt{k_1/k_{-1}}[\text{para-H}_2]^{3/2}$$

In comparison experimentally-determined rate law, $k_{obs} = k_2\sqrt{k_1/k_{-1}}$.

(2) Explain the difference between ortho-H₂ and para-H₂.

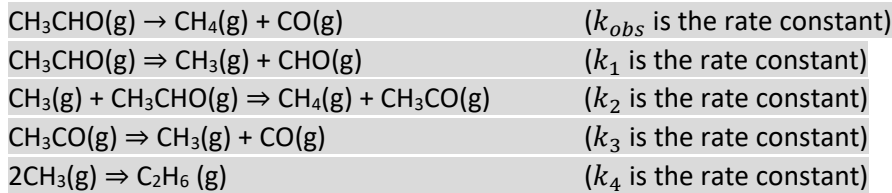
As given in the figure below, the difference is about the spin states of two H atoms. In the case of ortho-H₂, both H atoms have the same spin states (such as both have spin up states), which causes non-zero net spin in a molecule. On the other hand, in the case of para-H₂, two H atoms have different spin states, such as one has spin up state while the other has spin down state. As a result, the net spin in a molecule is 0. The para H₂ is more stable than the ortho-H₂ by 1.06 kJ/mol.

Spin isomers of molecular hydrogen



[Problem-VI: 17 pt → 14pt (6pt for (1), 8pt for (2))]

A proposed mechanism for the thermal decomposition of $\text{CH}_3\text{CHO}(\text{g})$ is



(1) Determine the rate laws for $\text{CH}_4(\text{g})$, $\text{CH}_3(\text{g})$, and $\text{CH}_3\text{CO}(\text{g})$.

*This means you write down $d[\text{CH}_4(\text{g})]/dt = \dots$, for example.

$$\frac{d[\text{CH}_4(\text{g})]}{dt} = k_2 [\text{CH}_3(\text{g})][\text{CH}_3\text{CHO}(\text{g})]$$

$$\frac{d[\text{CH}_3(\text{g})]}{dt} = k_1 [\text{CH}_3\text{CHO}(\text{g})] - k_2 [\text{CH}_3(\text{g})][\text{CH}_3\text{CHO}(\text{g})] + k_3 [\text{CH}_3\text{CO}(\text{g})] - 2k_4 [\text{CH}_3(\text{g})]^2$$

$$\frac{d[\text{CH}_3\text{CO}(\text{g})]}{dt} = k_2 [\text{CH}_3(\text{g})][\text{CH}_3\text{CHO}(\text{g})] - k_3 [\text{CH}_3\text{CO}(\text{g})]$$

(2) The rate law of the overall reaction (given by the first chemical equation) is given as follows:

$$\frac{d[\text{CH}_4(\text{g})]}{dt} = \left(\frac{k_1}{2k_4} \right)^{1/2} k_2 [\text{CH}_3\text{CHO}]^{3/2}$$

Assuming the steady-state approximate for CH_3 and $\text{CH}_3\text{CO}(\text{g})$, derive this rate law.

As the steady-state approximation

$$\frac{d[\text{CH}_3(\text{g})]}{dt} = 0$$

$$\frac{d[\text{CH}_3\text{CO}(\text{g})]}{dt} = 0$$

$$\frac{d[\text{CH}_3(\text{g})]}{dt} = k_1 [\text{CH}_3\text{CHO}(\text{g})] - k_2 [\text{CH}_3(\text{g})][\text{CH}_3\text{CHO}(\text{g})] + k_3 [\text{CH}_3\text{CO}(\text{g})] - 2k_4 [\text{CH}_3(\text{g})]^2$$

$$[\text{CH}_3\text{CO}(\text{g})]_{ss} = \frac{k_2}{k_3} [\text{CH}_3(\text{g})][\text{CH}_3\text{CHO}(\text{g})]$$

$$k_1 [\text{CH}_3\text{CHO}(\text{g})] - k_2 [\text{CH}_3(\text{g})]_{ss} [\text{CH}_3\text{CHO}(\text{g})] + k_3 [\text{CH}_3\text{CO}(\text{g})] - 2k_4 [\text{CH}_3(\text{g})]_{ss}^2 = 0$$

Replacing $[\text{CH}_3\text{CO}(\text{g})]$ with $[\text{CH}_3\text{CO}(\text{g})]_{ss}$, we have $k_1 [\text{CH}_3\text{CHO}(\text{g})] - 2k_4 [\text{CH}_3(\text{g})]_{ss}^2 = 0$

then $[\text{CH}_3(\text{g})]_{ss} = \left(\frac{k_1}{2k_4} \right)^{1/2} [\text{CH}_3\text{CHO}(\text{g})]^{1/2}$

Finally, applying this into $\frac{d[\text{CH}_4(\text{g})]}{dt} = k_2 [\text{CH}_3(\text{g})][\text{CH}_3\text{CHO}(\text{g})]$, we have

$$\frac{d[\text{CH}_4(\text{g})]}{dt} = k_2 [\text{CH}_3(\text{g})][\text{CH}_3\text{CHO}(\text{g})] \sim k_2 [\text{CH}_3(\text{g})]_{ss} [\text{CH}_3\text{CHO}(\text{g})] = k_2 \left(\frac{k_1}{2k_4} \right)^{1/2} [\text{CH}_3\text{CHO}(\text{g})]^{3/2}$$