Physical Chemistry
for Energy Engineering
(Homework-03 answers)

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*The class follows the text book: D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

HW03-01 [5pt in total]

[HW03-01] <Chapter-28: Chemical Kinetics I – Rate laws> 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.

(a) 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 $v(t) = -\frac{1}{\nu_A}\frac{d[A]}{dt} = -\frac{1}{\nu_B}\frac{d[B]}{dt} = \frac{1}{\nu_Y}\frac{d[Y]}{dt} = \frac{1}{\nu_Z}\frac{d[Z]}{dt}$. Then, the relationship between $v(t)$ and the concentrations of the reactants and the products is called the *rate law*. Rate laws can be determined from experimental measurements in general.

>> correct

HW03-01 [5pt in total]

[HW03-01] <Chapter-28: Chemical Kinetics I – Rate laws> 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.

(b) “reaction coordinate” 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, the reaction coordinate for the atomization reaction of a diatomic molecule is the bond length of the diatomic molecule. However, it is usually multi-dimensional and thus difficult to define it one-dimensionally in practice for general chemical reactions.

>> correct

HW03-01 [5pt in total]

[HW03-01] <Chapter-28: Chemical Kinetics I – Rate laws> 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.

(c) Consider a system involving reversible reaction, $A \rightleftharpoons B$. At equilibrium state, the concentrations of A and B should remain constant at their equilibrium values. It means “$-d[A]/dt = d[B]/dt = 0$”. In microscopic view, some A may be being changed to B and some B may be being changed to A even at an equilibrium state. However, there is no net change in the concentrations of either A or B, namely “dynamic equilibrium”.

>> correct

HW03-02 [5pt in total]

[HW03-02] 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.

(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 equilibrium constants (K_C), namely $K_C=k_1/k_{-1}$. It is called the "*principle of detailed balance*".

>> Wrong: This is true if the reactions are elementary reactions. But not necessarily true for normal (thus possibly complex) reactions.

HW03-02 [5pt in total]

[HW03-02] 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.

(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

HW03-02 [5pt in total]

[HW03-02] 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.

(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 $t_{1/2}$. In the case of first-order reactions, the half-life 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

HW03-02 [5pt in total]

[HW03-02] 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.

(d) The rate laws often have the form "$v(t) = k[A]^{m_A}[B]^{m_B} \cdots$", 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 "$\nu_A A + \nu_B B \rightarrow \nu_Y Y + \nu_Z Z$".

>> Wrong: that form is always true if the reaction is an elementary reaction. But usually, chemical reactions are complex reactions. In that case, that form is not necessarily appropriate (usually inappropriate) and thus the rate law should be determined by experiment.

HW03-02 [5pt in total]

[HW03-02] 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.

(e) In the activated-complex theory (transition state theory), it is considered the reactants and the "activated complex" ("transition state") are in equilibrium with each other and that we model the reaction by the two-step process "$A + B \rightleftharpoons AB^{\ddagger} \rightarrow P$". A+B are the reactant(s), which is also called the initial state. P is the product(s), which is also called the final state. $AB^{\ddagger}$ is the activated complex, which is also called the transition state and the intermediate.

>> Wrong: activated complex (transition state) is not reaction intermediate. The reaction intermediate is a concept in complex reaction, not the transition state theory. Indeed, in energy landscape, intermediates are generally located at local minima, while transition states are at saddle points.

HW03-03 [4pt in total]

[#03: $28-2] Di-nitrogen oxide, N_2O, decomposes according to the equation "$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$".
Under certain conditions at 900 K, the rate of reaction is 6.16×10^{-6} mol dm^{-3} s^{-1}.
Calculate the value of $d[N_2O]/dt$, $d[N_2]/dt$ and $d[O_2]/dt$.

According to the stoichiometry of the chemical equation, the rate of reaction is written as $v = -\frac{1}{2}\frac{d[N_2O]}{dt} = \frac{1}{2}\frac{d[N_2]}{dt} = \frac{d[O_2]}{dt}$. Thus, $\frac{d[N_2O]}{dt}$ = -1.23×10^{-5} mol dm^{-3} s^{-1}, $\frac{d[N_2]}{dt}$ = 1.23×10^{-5} mol dm^{-3} s^{-1}, and $\frac{d[O_2]}{dt}$ = 6.16×10^{-6} mol dm^{-3} s^{-1}.

HW03-04 [4pt in total]

[#04: $28-4] Define v, the rate of reaction, in terms of each of the reactants and products for the following reaction: $UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF$

According to the stoichiometry of the chemical equation, the rate of reaction is written as

$$v = -\frac{d[UF_6]}{dt} = -\frac{1}{2}\frac{d[H_2O]}{dt} = \frac{d[UO_2F_2]}{dt} = \frac{1}{4}\frac{d[HF]}{dt}.$$

HW03-05 [4pt in total]

[#05] Consider a reversible reaction: $\mathrm{A} \rightleftharpoons \mathrm{B}$, where k_1 and k_{-1} are the rate constants for forward and backward reactions, respectively. Assuming that the forward reaction is a first-order reaction of the reactant and the backward reaction is that of the product, derive a relationship among k_1, k_{-1} and K_C. K_C is the equilibrium constant regarding the concentration (not partial pressure).

According to the assumption, the rate laws are written as

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

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

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

HW03-06 [3pt each; 6pt in total]

[#06] Consider a reversible reaction: $\mathrm{A} \rightleftharpoons \mathrm{B}$, where k_1 and k_{-1} are the rate constants for forward and backward reactions, respectively.

(1) Assuming that the forward reaction is a second-order reaction of the reactant and the backward reaction is that of the product, derive a relationship among k_1, k_{-1} and K_C. K_C is the equilibrium constant regarding the concentration (not partial pressure).

According to the assumption, the rate laws are written as

$v_1 = -\frac{d[A]}{dt} = k_1[A]^2$ and $v_{-1} = -\frac{d[B]}{dt} = k_{-1}[B]^2$

At equilibrium state, $K_C = [B]_{eq}/[A]_{eq}$ and $v_1 = v_{-1}$ thus $k_1[A]_{eq}^2 = k_{-1}[B]_{eq}^2$.

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

HW03-06 [3pt each; 6pt in total]

[#06] Consider a reversible reaction: $\mathrm{A} \rightleftharpoons \mathrm{B}$, where k_1 and k_{-1} are the rate constants for forward and backward reactions, respectively.

(2) If the forward reaction is a first-order reaction of the reactant while the backward reaction is a second-order reaction of the product, what kind of relationship among k_1, k_{-1} and K_C is achieved?

According to the assumption,, the rate laws are written as

$v_1 = -\frac{d[A]}{dt} = k_1[A]$ and $v_{-1} = -\frac{d[B]}{dt} = k_{-1}[B]^2$

At equilibrium state, $K_C = [B]_{eq}/[A]_{eq}$ and $v_1 = v_{-1}$ thus $k_1[A]_{eq} = k_{-1}[B]_{eq}^2$. Hence, we cannot simply correlate the equilibrium constant and the rate constants. For example, we have $K_C = \frac{k_1/k_{-1}}{[B]_{eq}}$, which is dependent on $[B]_{eq}$.

HW03-07 [2pt each; 8pt in total]

[#07] We study "2HI(g) → H_2(g) + I_2(g)" assuming the backward reaction rarely takes place. We have two candidates of the rate law for this reaction: (i) "$v(t) = k[HI(g)]$" as a first-order reaction, and (ii) "$v(t) = k[HI(g)]^2$" as a second-order reaction. Using the experimental data on concentration change of HI given in the table below, please answer the following 3 questions. The initial conditions in the experiments were HI(g) = 1 mol dm^{-3}, H_2(g) = 0 mol dm^{-3}, I_2(g) = 0 mol dm^{-3} for each temperature.

(1) For the two candidate rate laws, please solve the differential equation so that the concentration change is described as a function of time.

For 1st order case, $v(t) = -\frac{1}{2}\frac{d[HI]}{dt} = \frac{d[H_2]}{dt} = \frac{d[I_2]}{dt} = k[HI]$

Hence, $[HI] = [HI]_0 e^{-2kt}$

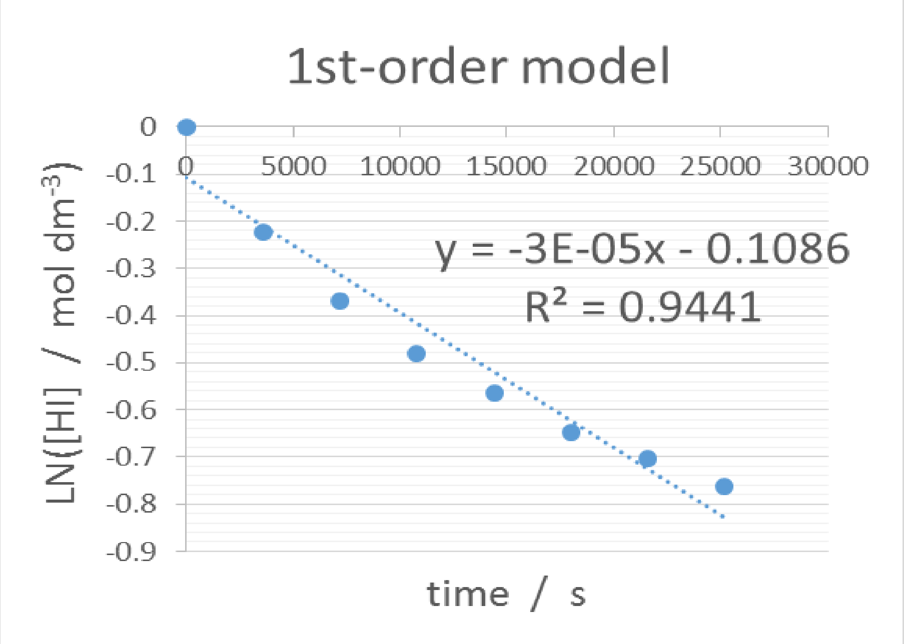
For 2nd order case, $v(t) = -\frac{1}{2}\frac{d[HI]}{dt} = \frac{d[H_2]}{dt} = \frac{d[I_2]}{dt} = k[HI]^2$

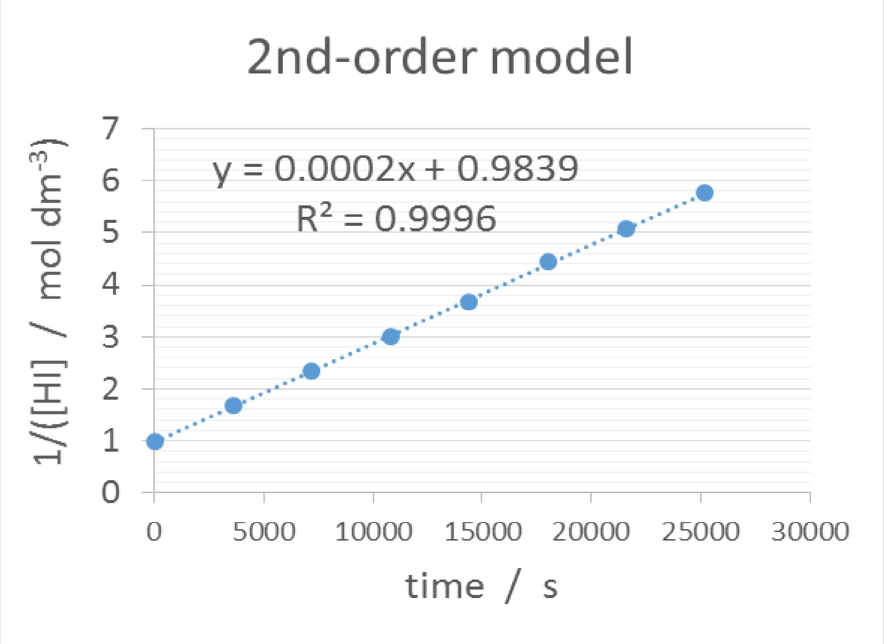
Hence, $\frac{1}{[HI]} = \frac{1}{[HI]_0} + 2kt$

HW03-07 [2pt each; 8pt in total]

(2) Determine which rate laws are more appropriate.

(2) For this assessment, we need to compare the agreement between the experimental data and theoretical data achieved by these two models. To see the difference clearly, we utilize the data of 650 K for this comparison, where the concentration of HI(g) is largely changed. From the figures below, it is clear that 2nd order model is more appropriate.





HW03-07 [2pt each; 8pt in total]

(3) Determine the rate constant (*k*) for each temperature. After least-square fitting, please assume that the significant figures are 3.

By least-square fitting, we can obtain the following rate constants at these temperatures.

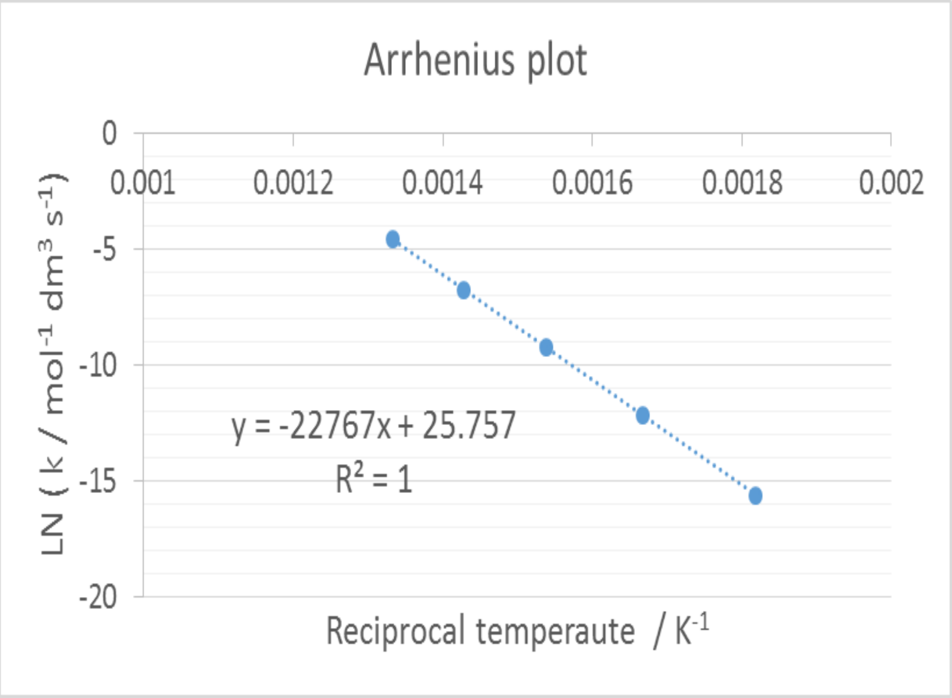
	550 K	600 K	650 K	700 K	750 K
$2k$ [mol^{-1} dm^{3} s^{-1}]	3.17E-07	1.05E-05	1.90E-04	2.27E-03	2.01E-02
k [mol^{-1} dm^{3} s^{-1}]	1.59E-07	5.25E-06	9.50E-05	1.14E-03	1.01E-02

HW03-07 [2pt each; 8pt in total]

(4) Assuming that the rate constants follow the Arrhenius equation, determine the activation energy and pre-exponential factor (frequency factor) by means of Arrhenius plot. After least-square fitting, please assume that the significant figures are 3.

Arrhenius equation is given as: $k(t) = Ae^{-E_a/RT}$, where k is the rate constant, A is the pre-exponential factor, and E_a is the activation energy. Taking logarithm makes it: $\ln(k) = \ln A - \frac{E_a}{RT}$. Thus, Arrhenius plot, where x axis is *1/T* and y axis is *ln(k)*, enables us to determine A and E_a. From the plot below, $\ln A =$ 25.757 and $-\frac{E_a}{R} = -22767$. Thus, $A =$1.54x10^{11} mol^{-1} dm^3 s^{-1} and

E_a = 189 kJ/mol = 1.96 eV.



HW03-08 [2pt each; 10pt in total]

[#08] We study "$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$" assuming the backward reaction rarely takes place. We have two candidates of the rate law for this reaction: (i) "$v(t) = k[NO(g)]$" as a first-order reaction, and (ii) "$v(t) = k[NO(g)][O_3(g)]$" as a second-order reaction (overall). Using the experimental data on concentration change of NO(g) given in the table below, please answer the following 5 questions. The initial conditions in the experiments were NO(g) = 1×10^{-6} mol dm^{-3}, $O_3(g)$ = 1×10^{-6} mol dm^{-3}, $NO_2(g)$ = 0 mol dm^{-3}, $O_2(g)$ = 0 mol dm^{-3} for each temperature.

(1) For the two candidate rate laws, please solve the differential equation so that the concentration change is described as a function of time.
*Hint: please use *"$[NO(g)] = [O_3(g)]$"* condition as in the performed experiments.

For 1st order case, $v(t) = -\frac{d[NO]}{dt} = k[NO]$

Hence, $[NO] = [NO]_0 e^{-kt}$

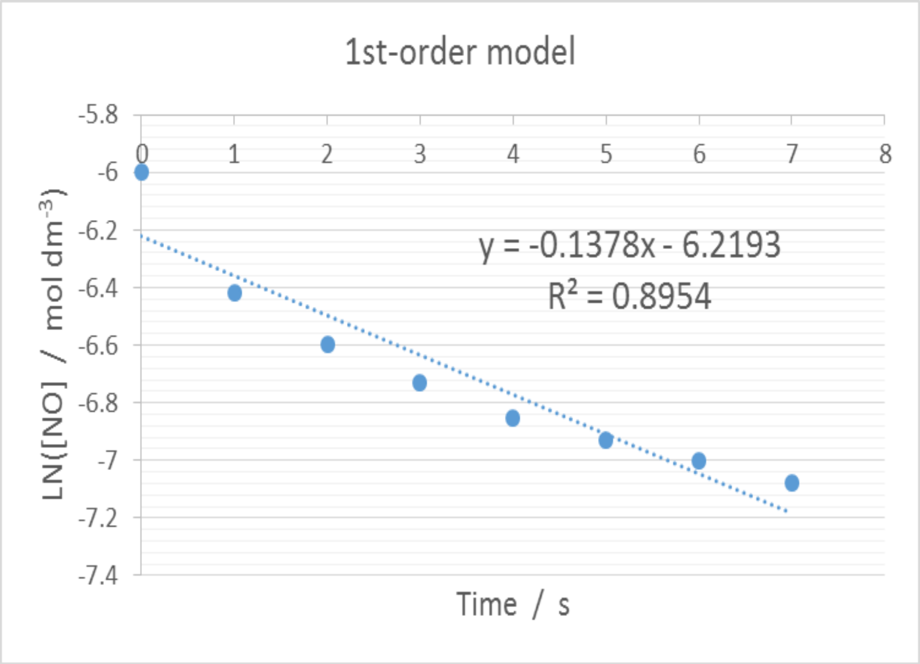
For 2nd order case, $v(t) = -\frac{d[NO]}{dt} = k[NO][O_3] = k[NO]^2$

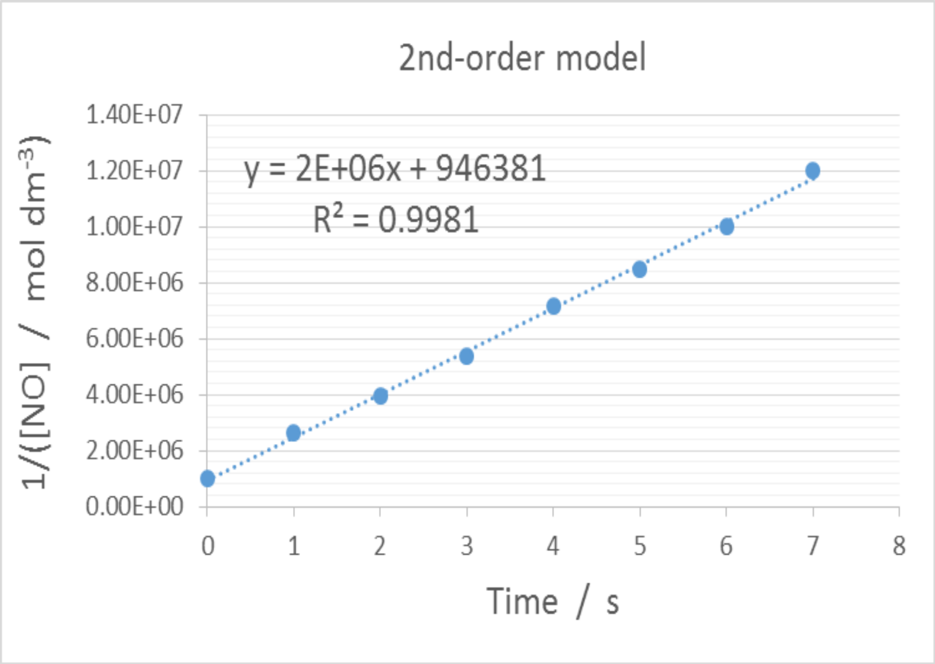
Hence, $\frac{1}{[NO]} = \frac{1}{[NO]_0} + kt$

HW03-08 [2pt each; 10pt in total]

(2) Determine which rate law is more appropriate.

(2) For this assessment, we need to compare the agreement between the experimental data and theoretical data achieved by these two models. To see the difference clearly, we utilize the data of 320 K for this comparison, where the concentration of NO(g) is largely changed. From the figures below, it is clear that 2nd order model is more appropriate.





HW03-08 [2pt each; 10pt in total]

(3) Determine the rate constant (*k*) for each temperature. After least-square fitting, please assume that the significant figures are 3.

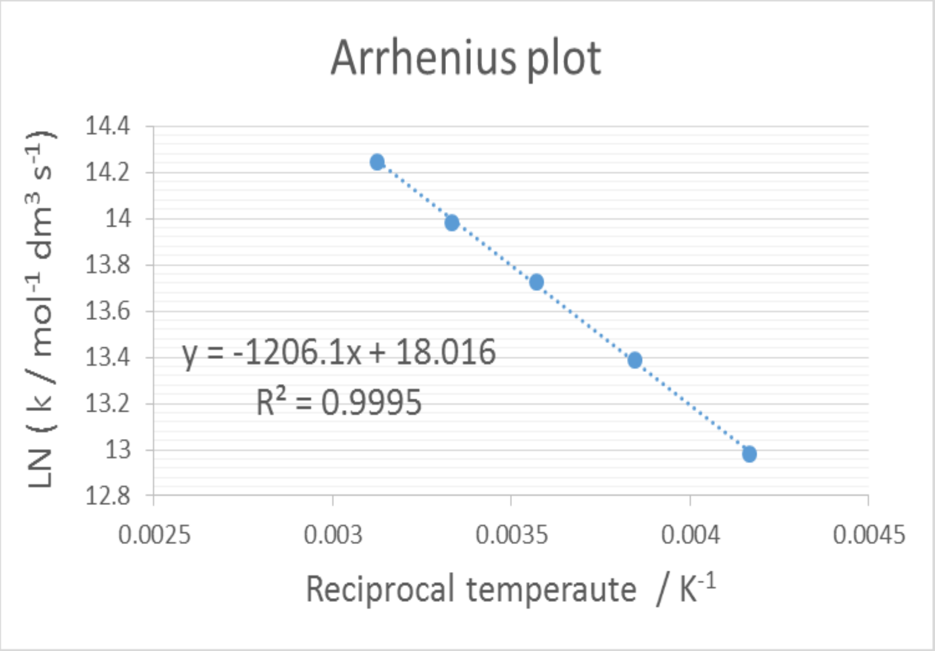
By least-square fitting, we can obtain the following rate constants at these temperatures.

	240 K	260 K	280 K	300 K	320 K
k [mol^{-1} dm^3 s^{-1}]	4.34E5	6.50E5	9.12E5	1.18E6	1.54E6

HW03-08 [2pt each; 10pt in total]

(4) Assuming that the rate constants follow the Arrhenius equation, determine the activation energy and pre-exponential factor (frequency factor) by means of Arrhenius plot. After least-square fitting, please assume that the significant figures are 3.

Arrhenius equation is given as: $k(t) = Ae^{-E_a/RT}$, where k is the rate constant, A is the pre-exponential factor, and E_a is the activation energy. Taking logarithm makes it: $\ln(k) = \ln A - \frac{E_a}{RT}$. Thus, Arrhenius plot, where x axis is *1/T* and y axis is *ln(k)*, enables us to determine A and E_a. From the plot below, $\ln A = 18.016$ and $-\frac{E_a}{R} = -1206.1$. Thus, A =6.67x10^7 mol^{-1} dm^3 s^{-1} and E_a = 10.0 kJ/mol = 0.104 eV.



HW03-08 [2pt each; 10pt in total]

(5) Discuss why the experimental conditions are largely different from the ones in #07 (temperatures, partial pressures of reactant(s), measurement time interval). If similar experimental conditions to #07 are used for #08, what kind of problems are brought?

*In this kind of question, please discuss as much as you can.

The difference mainly comes from the fact that rate constants are largely different between the two reactions. In the HW03-12 reaction, the activation energy is just 10 kJ/mol while HW03-11 reaction holds 190 kJ/mol. This difference introduces a large difference in the rate constants. For HW03-12 case, if such high temperature, as well as high pressure is utilized, the reaction is almost completed less than 1 s. We may shorten measurement time like 1 ns or 1 ps to pursuit the reaction at high temperatures. However, such experiment is not so easy.

In addition, if the measurement time interval of HW03-11 is applied to HW03-12 experiments, we need very accurate method to quantify the concentration. Hence, to accurately detect the concentration change with normal experimental setting, the given settings seemed to be utilized.

HW03-08 [2pt each; 10pt in total]

(5) Discuss why the experimental conditions are largely different from the ones in #07 (temperatures, partial pressures of reactant(s), measurement time interval). If similar experimental conditions to #07 are used for #08, what kind of problems are brought?

*In this kind of question, please discuss as much as you can.

(cont'd) Although HW03-12 settings are reasonable, we may need to recognize two points that may increase experimental error.

The first point is the temperature interval is just 20 K for HW03-12 experiment. So, we need more careful temperature controlling than HW03-11 experiment to make the error in temperature negligible. Note that if some heat is generated or some heat is absorbed by the reaction, temperature control may get difficult.

The second point is phase transition by lowering temperature. In these temperatures, no phase transition is expected as far as we check, but it is difficult to lower temperature more to make experiments easier.

HW03-09 [4pt in total]

[#09: $28-10] The Arrhenius activation energy and pre-exponential factor for the reaction "H(g) + Br_2(g) → HBr(g) + Br(g)" are 15.5 kJ $\mathrm{mol^{-1}}$ and 1.09×10^{11} $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$, respectively. Comparing with transition-state theory, please determine $\Delta^{\neq}H°$ (the standard enthalpy of activation) and $\Delta^{\neq}S°$ (the standard entropy of activation) at 1000 K. Please assume that the standard state is 1.00 mol $\mathrm{dm^{-3}}$ and the gasses behave as ideal gasses.

*Hint: $E_a = \Delta^{\ddagger}H° + 2RT$ and $A = \frac{e^2 k_B T}{hc^{\circ}} e^{\Delta^{\ddagger}S°/R}$. (You don't need to exactly remember these equations.)

The correlation between the Arrhenius parameters and $\Delta^{\neq}H°$ as well as $\Delta^{\neq}S°$ is as $E_a = \Delta^{\ddagger}H° + 2RT$ and $A = \frac{e^2 k_B T}{hc^{\circ}} e^{\Delta^{\ddagger}S°/R}$.

$\Delta^{\ddagger}H° = E_a - 2RT$ = -1.12 kJ $\mathrm{mol^{-1}}$

$\Delta^{\ddagger}S° = R\ln\left({Ahc^{\circ}}/{e^2 k_B T}\right)$ = -60.3J $\mathrm{mol^{-1}\ K^{-1}}$

HW03-10 [4pt in total]

[#10] The Arrhenius activation energy and re-exponential factor for the reaction "$2HI(g) \rightarrow H_2(g) + I_2(g)$" are 184 kJ mol^{-1} and 7.94x10^{10} dm^3 mol^{-1} s^{-1}, respectively. Comparing with transition-state theory, please determine $\Delta^{\neq}H°$ (the standard enthalpy of activation) and $\Delta^{\neq}S°$ (the standard entropy of activation) at 600 K. Please assume that the standard state is 1.00 mol dm^{-3} and the gasses behave as ideal gasses. Then, please check the sign of $\Delta^{\neq}S°$ and explain the physical meaning of it.

As the same with #09, $\mathit{\Delta}^{\ddagger}H° =$174 kJ mol^{-1}, $\mathit{\Delta}^{\ddagger}S° =$ -58.7J mol^{-1} K^{-1}.

The entropy reflects the degree of disorder. In this case, $\mathit{\Delta}^{\ddagger}S° < 0$ means the activated complex structure is more ordered than the reactants.
Regarding the structure, the activated complex would be regarded as 1 molecule weakly bound, like H-I···H-I. The combined molecule is more "condensed". Then, in analogy with the entropy difference between gas and liquid, 1 combined molecule should have lower entropy than 2 separated molecules.

HW03-11 [5pt in total]

<Chapter-29: Chemical Kinetics II – Reaction Mechanics>
[#11] 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.

(a) Most chemical reactions involve one or multiple intermediates, and the overall kinetic process can be written as: *reactant(s)* → *intermediate(s)* → *product(s).* On the other hand, an "*elementary reaction*" does not involve an intermediate.

>> correct

HW03-11 [5pt in total]

<Chapter-29: Chemical Kinetics II – Reaction Mechanics>
[#11] 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.

(b) A chemical reaction that does not involve any intermediates and thus occurs in a single step is called "*elementary reaction*", *while that involves* some intermediate(s) is called "*complex reaction*". When we need to distinguish these two types of reactions, ⟶ and ⟵ are used for elementary reactions, while ⇒ and ⇐ for complex reactions. Any complex reactions can be decomposed to multiple elementary reactions.

>> Wrong: ⇒ and ⇐ for elementary reactions, and ⟶ and ⟵ for complex reactions.

HW03-11 [5pt in total]

<Chapter-29: Chemical Kinetics II – Reaction Mechanics>
[#11] 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.

(c) A catalyst is a substance that participates in the concerned chemical reaction but is not consumed in the reaction. A catalyst provides a new reaction mechanism, and usually it is of a smaller reaction barrier (activation energy). As reaction rate depends exponentially on the activation barrier, even a small change in the barrier results in a substantial change in the reaction rate.

>> correct

HW03-11 [5pt in total]

<Chapter-29: Chemical Kinetics II – Reaction Mechanics>
[#11] 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.

(d) A "chain reaction" is a sequence of reactions where a reactive product or by-product causes additional reactions to take place. Some elementary reactions involved in a chain reaction may retard the reaction from proceeding overall.

>> correct

HW03-12 [5pt in total]

[#12] 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.

(a) For an elementary reaction, if the chemical equation is written as "*a A + b B* → *products*" (more precisely, "*a A + b B* ⇒ *products*"), the rate law is written as "$\mathrm{v(t) = k[A]^a[B]^b}$". On the other hand, if the chemical reaction is a complex reaction, the rate law cannot be defined so simply in most cases.

>> correct

HW03-12 [5pt in total]

[#12] 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.

(b) If one step in a reaction mechanism is much faster than any of the other steps, that fast step effectively controls the overall reaction rate and is called the rate-determining step (or rate-controlling step).

>> Wrong: not “much faster” but “much slower”. The slower one may become a rate-determining step (rate-controlling step).

HW03-12 [5pt in total]

[#12] 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.

(c) Because a catalyst is not consumed, the exothermicity or endothermicity of the chemical reaction is not affected. In other words, the catalyst just provide another reaction path, which usually has a lower barrier for the reaction than the original path, while it does not change the (molar) enthalpy of reaction nor the (molar) Gibbs energy of reaction.

>> correct

HW03-12 [5pt in total]

[#12] 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.

(d) For reaction “$\mathrm{A} \overset{k_1}{\Rightarrow} \mathrm{I} \overset{k_2}{\Rightarrow} \mathrm{P}$”, if $k_1 \gg k_2$, we can reasonably make the approximation that $\mathrm{d}[I]/dt = 0$, which is called the steady-state approximation and can greatly simplify the mathematics associated with a particular kinetic model.

>> Wrong: $k_1 \gg k_2$ should be $k_2 \gg k_1$.

HW03-13 [4pt in total]

[#13: $29-2] Determine the rate law for the reaction *“F(g) + D$_2$(g) ⇒ FD(g) + D(g)”* with the rate constant k. Give the units of k. And determine the molecularity of this reaction.

Because it is an elementary reaction,

$$v = -\frac{d[F]}{dt} = -\frac{d[D_2]}{dt} = \frac{d[FD]}{dt} = \frac{d[D]}{dt} = k[F][D_2]$$

As two molecules are involved as the reactants in this elementary reaction, the molecularity is 2.

The unit of k is [mol^{-1} m^3 s^{-1}], [mol^{-1} dm^3 s^{-1}], etc.

HW03-14 [5pt in total]

[#14: $29-3] Determine the rate law for the reaction *"$I(g) + I(g) + M(g) \Rightarrow I_2(g) + M(g)$"* with the rate constant k, where M is any molecule present in the reaction container. Give the units of k. Determine the molecularity of this reaction. Is this reaction identical to *"$I(g) + I(g) \Rightarrow I_2(g)$"* ? Explain it.

Because it is an elementary reaction,

$$v = -\frac{1}{2}\frac{d[I]}{dt} = \frac{d[I_2]}{dt} = k[I]^2[M]$$

As three molecules are involved as reactants in this elementary reaction, the molecularity is 3. The unit of k is [$\mathrm{mol^{-2}\ m^{6}\ s^{-1}}$], [$\mathrm{mol^{-2}\ dm^{6}\ s^{-1}}$], etc.

In the case of *"$I(g) + I(g) \Rightarrow I_2(g)$"*, the rate law becomes:

$$v = -\frac{1}{2}\frac{d[I]}{dt} = \frac{d[I_2]}{dt} = k[I]^2$$

The molecularity of this reaction is 2. The first reaction requires the collision of 3 molecules, while this one 2 molecules. So, the mechanisms not identical each other.

HW03-15 [5pt in total]

[#15: $29-9] The reaction mechanism of "A+B→P" is:

A+B $\underset{\Leftarrow}{\overset{\Rightarrow}{}}$ C (k_1 is the rate constant for the forward reaction,
and k_{-1} for the backward)

C ⇒ P (k_2 is the rate constant)

Write the expression for $d[P]/dt$, the rate of product formation. Assume equilibrium is established in the first reaction before any appreciable amount of product is formed, and thereby show that

$$d[P]/dt = k_2 K_c [A][B]$$

where K_c is the equilibrium constant for step(1) of the reaction mechanism. This assumption is called the *fast-equilibrium approximation*.

The rate law of the second reaction is: $v = d[P]/dt = k_2[C]$.

According to the fast-equilibrium approximation, we can consider the first reaction is always at equilibrium, $K_c = {}^{[C]}\!/_{[A][B]}$. Because $v_1 (= k_1[A][B]) = v_{-1} (= k_{-1}[C])$, which is achieved at equilibrium, should be also always fulfilled, $K_c = {}^{[C]}\!/_{[A][B]} = {}^{k_1}\!/_{k_{-1}}$

Applying this equation to the rate law, $d[P]/dt = k_2[C] = k_2 K_c [A][B] = \frac{k_1 k_2}{k_{-1}}[A][B]$.

HW03-16 [5pt in total]

[#16: $29-10] The experimentally-observed rate law for the reaction of para-hydrogen to ortho-hydrogen

para-H_2(g) → ortho-H_2(g) (k_{obs} is the rate constant)

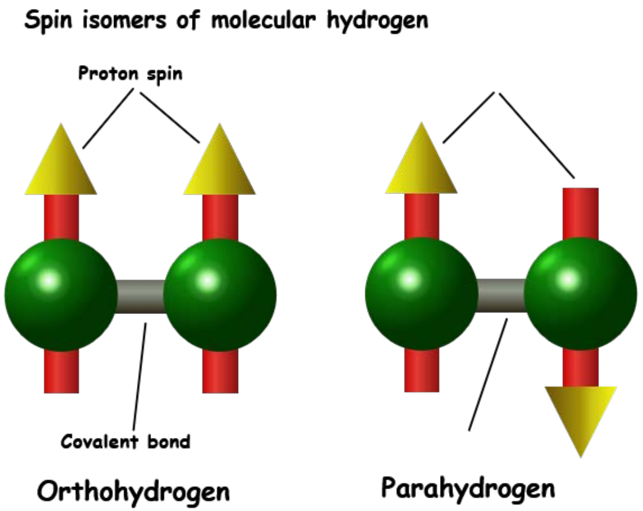
is $d[ortho-H_2]/dt = k_{obs}[para-H_2]^{3/2}$

The following mechanism is proposed:

para-H_2(g) $\underset{\Leftarrow}{\overset{\Rightarrow}{}}$ 2H(g) (k_1 for the forward, and k_{-1} for the backward)

H(g) + para-H_2(g) ⇒ ortho-H_2(g) + H(g) (k_2 is the rate constant)

Please consider that "para-H_2(g) $\underset{\Leftarrow}{\overset{\Rightarrow}{}}$ 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.



Para H_2 is more stable than ortho H_2 by 1.06 kJ/mol

https://en.wikipedia.org/wiki/Spin_isomers_of_hydrogen

HW03-16 [5pt in total]

The rate law of the 2nd reaction is: $v = d[ortho - H_2]/dt = k_2[H][para - H_2]$.

The equilibrium constant is defined as $K_c = {[H]_{eq}}^2/[para-H_2]_{eq}$.

Because $v_1 (= k_1[para - H_2]_{eq}) = v_{-1} (= k_{-1}{[H]_{eq}}^2)$ is achieved at equilibrium, $K_c = k_1/k_{-1}$ is obtained.

Applying this equation and the first equilibrium approximation, namely $K_c = [H]^2/[para-H_2]$, to the rate law,

$$d[ortho - H_2]/dt = k_2[H][para - H_2] = k_2\sqrt{K_c}[para - H_2]^{3/2}$$

$$= k_2\sqrt{k_1/k_{-1}}\,[para - H_2]^{3/2}$$

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

HW03-17 [5pt in total]

[#17: $29-17] The rate law for the reaction described by

$2H_2(g) + 2NO(g) \rightarrow N_2(g) + 2H_2O(g)$ (k_{obs} is the rate constant)

is $d[N_2]/dt = k_{obs}[H_2][NO]^2$

Below is a proposed mechanism for this reaction

$H_2(g) + NO(g) + NO(g) \Rightarrow N_2O(g) + H_2O(g)$ (k_1 is the rate constant)

$H_2(g) + N_2O(g) \Rightarrow N_2(g) + H_2O(g)$ (k_2 is the rate constant)

Under what conditions does this mechanism give the observed rate law? Express k_{obs} in terms of the rate constant for the individual steps of the mechanism.

The rate law is described based on the second step:

$$d[N_2]/dt = k_2[H_2][N_2O]$$

We assume the steady-state approximation can be used for N_2O, considering $k_2 \gg k_1$ because the second reaction is of bi-molecules while the first reaction is of tri-molecules.

$$d[N_2O]/dt = k_1[H_2][NO]^2 - k_2[H_2][N_2O] = 0$$

$$[N_2O] = (k_1/k_2)[NO]^2$$

Applying this result to the rate law of the overall reaction:

$$d[N_2]/dt = k_2[H_2] \times (k_1/k_2)[NO]^2 = k_1[H_2][NO]^2$$

Thus, $k_{obs} = k_1$

HW03-18 [6pt in total]

[#18: $29-18)] A second proposed mechanism for the reaction discussed in [#17] is

$NO(g) + NO(g) \underset{\Leftarrow}{\overset{\Rightarrow}{}} N_2O_2(g)$ (k_1 for the forward, and k_{-1} for the backward)

$H_2(g) + N_2O_2(g) \Rightarrow N_2O(g) + H_2O(g)$ (k_2 is the rate constant)

$H_2(g) + N_2O(g) \Rightarrow N_2(g) + H_2O(g)$ (k_3 is the rate constant)

Under what conditions does this mechanism give the observed rate law? Express k_{obs} in terms of the rate constant for the individual steps of the mechanism. Do you favor this mechanism or that given in [#17]. Explain your reasoning.

*Hint: you can use the steady-state approximation for N_2O. In addition, you can assume that the fast equilibrium is established in the first step.

First, we assume that k_1 and k_{-1} are adequately larger than k_2, thus we can assume that the equilibrium of the first step is achieved before the 2nd and 3rd steps proceed, namely the fast equilibrium approximation. For this condition, we can consider the equilibrium of the 1st step neglecting 2nd and 3rd steps. Hence,

$$v_1(= k_1[NO]^2) = v_{-1}(= k_{-1}[N_2O_2]), \qquad K_C = \frac{[N_2O_2]}{[NO]^2} = \frac{k_1}{k_{-1}}$$

HW03-18 [5pt in total]

Here, we write down all rate laws:

$$\frac{d[N_2O_2]}{dt} = k_1[NO]^2 - k_{-1}[N_2O_2] - k_2[H_2][N_2O_2], \quad \frac{d[NO]}{dt} = -2k_1[NO]^2$$

$$\frac{d[N_2]}{dt} = k_3[H_2][N_2O], \quad \frac{d[H_2]}{dt} = -k_2[H_2][N_2O_2] - k_3[H_2][N_2O]$$

$$\frac{d[N_2O]}{dt} = k_2[H_2][N_2O_2] - k_3[H_2][N_2O], \quad \frac{d[N_2]}{dt} = k_3[H_2][N_2O]$$

In addition, we assume that $k_3 \gg k_2$ so that we can employ the steady-state approximation in respect to N_2O: $d[N_2O]/dt = 0$. Thus,

$$k_2[H_2][N_2O_2] - k_3[N_2O][H_2] = 0, \quad k_2[N_2O_2] = k_3[N_2O]$$

Then, $\frac{d[N_2]}{dt} = k_3[H_2][N_2O] = k_2[H_2][N_2O_2] = k_2[H_2]\frac{k_1}{k_{-1}}[NO]^2 = \frac{k_1k_2}{k_{-1}}[H_2][NO]^2$

Thus, also this model can explain the experimentally observed rate law, with $k_{obs} = \frac{k_1k_2}{k_{-1}}$. To achieve this, we need to assume (1) k_1 and k_{-1} are adequately larger than k_2, and (2) $k_3 \gg k_2$.

In comparison with the model given in HW03-22, the model of HW03-23 would be more promising because all elementary reactions are up to bi-molecular reaction. The tri-molecular elementary reaction in HW03-22 should significantly lower the reaction rate of this mechanism.

HW03-19 [5pt in total]

[#19] (1) We consider a reaction among N_2(g), O_2(g) and NO(g) under a constant pressure condition. In a reaction system, 2.00 moles of N_2 and 3.00 moles O_2 are initially introduced. Please evaluate the amount (in mol) of each species (N_2(g), O_2(g) and NO(g)) at equilibrium state of 1.00 bar and 5000 K. The equilibrium constant at 5000 K is given as $\mathrm{Kp(T)} = 96.0$ for "$\mathrm{N_2(g) + O_2(g)} \rightleftharpoons \mathrm{2NO(g)}$". If needed, please use $2^{1/2} = 1.414$.

The amount of each gaseous species are:

	N_2	O_2	NO
Initial	2 [mol]	3[mol]	0 [mol]
At equilibrium	2-ξ [mol] ⇒ (2-ξ)/5 [bar]	3- ξ [mol] ⇒ (3- ξ)/5 [bar]	2ξ [mol] ⇒ 2ξ/5 [bar]

$$K_P = 96.0 = \frac{[NO/1bar]^2}{[N_2/1bar][O_2/1bar]} = \frac{[2\xi/5]^2}{[(2-\xi)/5][(3-\xi)/5]} = \frac{4\xi^2}{(2-\xi)(3-\xi)}$$

$$4\xi^2 = K_P(2-\xi)(3-\xi) = K_P(\xi^2 - 5\xi + 6), \quad (K_P - 4)\xi^2 - 5K_P\,\xi + 6K_P = 0$$

$$\xi = \frac{5K_P \pm \sqrt{25K_P{}^2 - 4(K_P - 4)6K_P}}{2(K_P - 4)} = \frac{5K_P \pm \sqrt{K_P{}^2 + 96K_P}}{2(K_P - 4)} = \frac{K_P(5 \pm \sqrt{2})}{2(K_P - 4)} = 1.87\ [\mathrm{mol}]$$

Hence

N_2	O_2	NO
0.13 [mol]	1.13 [mol]	3.74 [mol]

HW03-19 [5pt in total]

(2) Our system is at an equilibrium state of 1.00 bar and 5000 K as determined above. We would like to decompose NO (to N_2 and O_2) more. So, please give some ideas to make it in the following 2 cases.

(case-i) You have a device to introduce $N_2(g)$ or/and $O_2(g)$ into the system with keeping the system volume constant. How you can decompose NO more in this case.

*You can introduce (1) some $N_2(g)$, (2) some $O_2(g)$, or (3) "some $N_2(g)$ and some $O_2(g)$" into the system.

(case-ii) You have a device to remove $N_2(g)$ or/and $O_2(g)$ from the system with keeping the system volume constant. How you can decompose NO more in this case.

*You can remove (1) some $N_2(g)$, (2) some $O_2(g)$, or (3) "some $N_2(g)$ and some $O_2(g)$" from the system.

$$K_P = 96.0 = \frac{\left[\frac{NO}{1bar}\right]_{eq}^2}{\left[\frac{N_2}{1bar}\right]_{eq}\left[\frac{O_2}{1bar}\right]_{eq}} = \frac{\left(\frac{3.74}{5}\right)^2}{\left(\frac{0.129}{5}\right)\left(\frac{1.13}{5}\right)}$$

$\Longrightarrow\Longrightarrow$ (+α mol N_2; +β mol O_2; then variation of ξ mol to get an equilibrium) $\Longrightarrow\Longrightarrow$

$$\frac{((3.74+2\xi)/(5+\alpha+\beta))^2}{\big((0.129-\xi+\alpha)/(5+\alpha+\beta)\big)\big((1.13-\xi+\beta)/(5+\alpha+\beta)\big)} = \frac{(3.74+2\xi)^2}{((0.129-\xi+\alpha))((1.13-\xi+\beta))}$$

HW03-19 [3pt each; 6pt in total]

(+α mol N_2; +β mol O_2; then variation of ξ mol to get an equilibrium)

$$\frac{(3.74 + 2\xi)^2}{((0.129 - \xi + \alpha))((1.13 - \xi + \beta))}$$

(case-i) If we introduce some amount of N_2 or/and O_2, the denominator is increased. To compensate it, the system moves to (1) decreasing denominator or (2) increasing numerator. Both are achieved by $\xi > 0$, which means that the amount of NO is increased. Hence, we cannot decompose NO more by adding N_2 and/or O_2.

(case-ii) If we remove some amount of N_2 or/and O_2, the denominator is decreased. To compensate it, the system moves to (1) increasing denominator or (2) decreasing numerator. Both are achieved by $\xi < 0$, which means that the amount of NO is decreased, thus NO is decomposed. Hence, we can decompose NO more by removing N_2 and/or O_2. If N_2 or/and O_2 are continuously taken out from the reaction system, finally all NO is decomposed. Regarding the efficiency, if a fixed amount is taken, taking out N_2 decreases the denominator more than taking out O_2, thus more decompose NO.