

CHEMICAL REACTOR DESIGN

CHENG 323

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Lecture 11

Prepared by: Dr Shaker Haji - CHENG 323

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3 Rate Laws and Stoichiometry

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In this Chapter

In Chapter 2, if $-r_A$ vs. X data are available, we can calculate the reactor volume necessary to achieve a specified X for flow systems or the time to achieve a given X in a batch system.

In this chapter we will show how to obtain $-r_A = f(X, T)$ as oppose to $-r_A$ vs. X data.

This relationship between $-r_A$ and X will be obtained in two steps:

1. We define the rate law, which relates $-r_A = f(C_i, T, \dots \text{etc})$.
2. We develop a stoichiometric table so that one can write $C_i = f(X)$.

Combining steps 1 and 2, we see that one can then write $-r_A = f(X, T)$, then use the techniques in Chapter 2 to design reaction systems.

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3 Rate Laws and Stoichiometry

Part 1: Rate Laws

Part 1: Rate Laws

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3.1 Basic Definitions

□ **Elementary Reaction:**

An *elementary reaction* is one that involves a single step reaction.

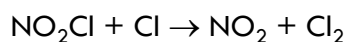
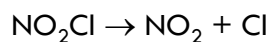
e.g., the collision between two identical molecules leading directly to the products: $2 \text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$

□ **Non-Elementary Reaction:**

A *non-elementary reaction* is one that involves series of reaction steps.

e.g., $2 \text{NO}_2\text{Cl} \rightarrow 2 \text{NO}_2 + \text{Cl}_2$

The actual mechanism for the above rxn is the following two-step sequence of elementary reactions:

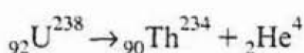


Ref: Chemistry by J. Brady et al.

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3.1 Basic Definitions

- The **molecularity** of a rxn is the number of atoms, ions, or molecules involved through collisions in a rxn step.
- The terms unimolecular, bimolecular, & termolecular refer to rxns involving, respectively, one, two, or three atoms (or molecules) interacting or colliding in any one rxn step.
- The most common example of a unimolecular rxn is radioactive decay, e.g.:



Uranium (238.0508) → Thorium (234.0436) + Helium (4.0026)

Mass: 238.0508 g 238.0462 g $\Delta m = -4.6 \text{ mg}$

- The rate of disappearance of uranium (U) is given by the rate law:

$$-r_{\text{U}} = k_{\text{U}} C_{\text{U}}$$

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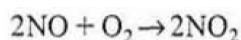
3.1 Basic Definitions

- The true bimolecular rxns that exist are usually reactions involving free radicals such as $\text{Br} \cdot + \text{C}_2\text{H}_6 \rightarrow \text{HBr} + \text{C}_2\text{H}_5 \cdot$

with the rate of disappearance of bromine given by the rate law

$$-r_{\text{Br}} = k C_{\text{Br}} C_{\text{C}_2\text{H}_6}$$

- The probability of a termolecular rxn occurring – in a single step – is almost nonexistent, e.g.:



- In most instances the reaction pathway in a termolecular rxn follows a series of bimolecular reactions.
- The rxn pathway involves active intermediate complexes.

[Continue Reading @ home](#)

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3.1 Basic Definitions

□ *Homogeneous Reaction:*

A *homogeneous reaction* is one that involves only one phase.

□ *Heterogeneous Reaction:*

A *heterogeneous reaction* involves more than one phase, and the reaction usually occurs at the interface between the phases.

□ *Irreversible Reaction:*

An *irreversible reaction* is one that proceeds only in one direction and continues in that direction until the limiting reactant is consumed.

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3.1 Basic Definitions

□ *Reversible Reaction:*

A *reversible reaction* can proceed in either direction, depending on the concentrations of reactants and products relative to the corresponding equilibrium concentrations.

	$C_{T0}=C_T=1\text{ M}$	A	$\leftrightarrow$	B		rxn direction
	Equilibrium Conc. (M)	0.7		0.3	$K_c=0.43$	N/A
1	Initial Conc. (experiment 1)	1.0		0.0	$Q=0$	
2	Initial Conc. (experiment 2)	0.2		0.8	$Q=4$	

K_c : concentration equilibrium constant, Q : reaction quotient

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3.1 Basic Definitions

□ Reversible Reaction:

A reversible reaction can proceed in either direction, depending on the concentrations of reactants and products relative to the corresponding equilibrium concentrations.

- Strictly speaking, **no** chemical reaction is completely irreversible.
- However, for many rxns, the equilibrium point lies so far to the product side that these rxns are treated as irreversible rxns.

$C_{T0} = C_T = 1 \text{ M. } T = 30^\circ\text{C}$	A	$\leftrightarrow$	B	+ Heat	comments
Equilibrium Conc. (M)	0.01		0.99	$K_c = 99$	Reaction: · written $A \rightarrow B$ · said to be irreversible

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3.1.1 Relative Rates of Reaction



For the rxn $a A + b B \longrightarrow c C + d D$, write the rates of rxn of B, C, & D relative to $-r_A$.

Answer:

$$-r_B = \left(\frac{b}{a}\right)(-r_A), \quad r_C = \left(\frac{c}{a}\right)(-r_A), \quad r_D = \left(\frac{d}{a}\right)(-r_A)$$

The relative rates can be conveniently written as:

$$\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d}$$

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3.1.1 Relative Rates of Reaction

For the rxn $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$, write the rates of rxn relative to each other.

Answer:

If $r_{\text{NO}_2} = 4 \text{ mol}/(\text{m}^3\cdot\text{s})$, calculate the rate of disappearance of O_2 & NO .

Answer:

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3.1.1 Relative Rates of Reaction

For the rxn $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$, write the rates of rxn relative to each other.

Answer:

$$\frac{r_{\text{NO}}}{-2} = \frac{r_{\text{O}_2}}{-1} = \frac{r_{\text{NO}_2}}{2}$$

If $r_{\text{NO}_2} = 4 \text{ mol}/(\text{m}^3\cdot\text{s})$, calculate the rate of disappearance of O_2 & NO .

Answer: $-r_{\text{NO}} = 4 \text{ mol}/(\text{m}^3\cdot\text{s})$ & $-r_{\text{O}_2} = 2 \text{ mol}/(\text{m}^3\cdot\text{s})$

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3.2 The Reaction Order and the Rate Law

The rate of disappearance of A, $-r_A$, mainly depends on composition and temperature.

For many reactions, it can be written as the product of a reaction rate constant k_A , and a function of the concentrations (activities) of the various species involved in the reaction:

$$-r_A = [k_A(T)][f(C_A, C_B, \dots)]$$

The algebraic equation that relates $-r_A$ to the species concentrations is called the kinetic expression or **rate law**.

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3.2.0 The Specific Rate of Reaction (Rate Constant)

The specific rate of rxn (also called the **rate constant**), k_A , like the rxn rate, $-r_A$, always refers to a particular species in the rxn.

Example: $A \rightarrow 2B$, we write $-r_A = k_A C_A$ or $r_B = k_B C_A$

The k is normally subscripted with respect to the basis species, k_A .

For the rxn $a A + b B \longrightarrow c C + d D \implies \frac{k_A}{a} = \frac{k_B}{b} = \frac{k_C}{c} = \frac{k_D}{d}$

For the rxn $A \rightarrow 2B$, $k_A/1 = k_B/2$ or $k_B = 2 k_A$

For the rxn $1\text{NaOH} + 1\text{HCl} \rightarrow 1\text{NaCl} + 1\text{H}_2\text{O}$, all the rate constants are equal: $k = k_{\text{NaOH}} = k_{\text{HCl}} = k_{\text{NaCl}} = k_{\text{H}_2\text{O}}$

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3.2.1 Power Law Models and Elementary Rate Laws

How the $f(C_A, C_B, \dots)$ is determined?

$$-r_A = [k_A(T)][f(C_A, C_B, \dots)]$$

The dependence of the $-r_A$ on the C_i is almost without exception determined by experimental observation.

Although the functional dependence on C_i may be postulated from theory, experiments are necessary to confirm the proposed form.

One of the most common forms of this dependence is the **Power Law Model**.

Here the rate law is proportional to the product of concentrations of the individual reacting species, each of which is raised to a power.

For example, for the rxn $a A + b B \rightarrow c C$: $-r_A = k_A C_A^\alpha C_B^\beta$

If the powers in the rate law are identical to the stoichiometric coefficients in the rxn (e.g., $\alpha=a$ & $\beta=b$), then the **rate law** is said to be **elementary**.

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The Rate Law of an Elementary Reaction

- The reaction rate of an **elementary reaction** is proportional to the concentration of each of the involved reactants.
- Therefore, the powers in the power law model are identical to the stoichiometric coefficients of the reactants.
- i.e., if the rxn $a A + b B \rightarrow c C$ was elementary, then its rate law would be

$$-r_A = k_A C_A^a C_B^b$$

- Example: For the elementary rxn: $O \bullet + CH_3OH \rightarrow CH_3O \bullet + OH \bullet$, the rate law is:

$$-r_O = k(C_O)(C_{CH_3OH})$$

- **Conclusion:** ALL elementary rxns HAVE elementary rate laws
but NOT ALL elementary rate laws REPRESENT elementary rxns

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Elementary & Non-Elementary Reactions & Rate Laws

- The rate law of the *non-elementary rxn* $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ was experimentally found to be

$$-r_{\text{NO}} = k_{\text{NO}} C_{\text{NO}}^2 C_{\text{O}_2}$$

- For this non-elementary rxn, the powers = stoichiometric coefficient!!!
- Consequently:
 - The rate law is said to be an *elementary rate law*, since powers = stoichiometry.
 - The reaction is said to *follow an elementary rate law*, but the rxn is not elementary by itself.

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3.2.1 Elementary & Non-Elementary Rate Laws



Reaction	Elementary Reaction?	Rate Law	Elementary Rate Law?	Comments
$2\text{NO}_2 \rightarrow \text{NO}_3 + \text{NO}$	Yes	$-r_{\text{NO}_2} = k_{\text{NO}_2} C_{\text{NO}_2}^2$	Yes	power = stoichiometric co.
$2\text{NO}_2\text{Cl} \rightarrow 2\text{NO}_2 + \text{Cl}_2$	No	$-r_{\text{NO}_2\text{Cl}} = k C_{\text{NO}_2\text{Cl}}$	No	power $\neq$ stoichiometric co.
$2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$	No	$-r_{\text{NO}} = k_{\text{NO}} C_{\text{NO}}^2 C_{\text{O}_2}$	Yes	non-elementary, termolecular rxn rxn follows an elementary rate law
$\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$	No	$-r_{\text{CO}} = k C_{\text{CO}} C_{\text{Cl}_2}^{1.5}$	No	power $\neq$ stoichiometric co.
$\text{C}_6\text{H}_5\text{CH}_3 + \text{H}_2 \rightarrow \text{C}_6\text{H}_6 + \text{CH}_4$ $\text{T} + \text{H}_2 \rightarrow \text{B} + \text{M}$	No	$-r'_{\text{T}} = \frac{k P_{\text{H}_2} P_{\text{T}}}{1 + K_{\text{B}} P_{\text{B}} + K_{\text{T}} P_{\text{T}}}$	No	Langmuir-Hinshelwood kinetics K_{B} & K_{T} are adsorption equ. constants and k is the rate constant

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Elementary & Non-Elementary Reactions & Rate Laws

30 min

Study the rest of the slides at home.

Solve the following [exercise](#) now.

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Reaction Order

$-r_A = k_A C_A^\alpha C_B^\beta$

The exponents of the concentrations lead to the concept of **reaction order**.

In the above rate law, the rxn is α order with respect to reactant A, and β order w.r.t. reactant B.

The overall order of the reaction is n , where $n = \alpha + \beta$

Consider a reaction with $-r_A = k_A C_A^n$, what are the units of k_A ?

$k_A = \frac{(\text{Concentration})^{1-n}}{\text{Time}}$

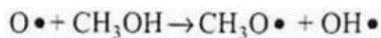
Rxn Order	Rxn Law	Units of k_A
Zero-order, $n=0$	$-r_A = k_A$	mol/L.s
First-order, $n=1$	$-r_A = k_A C_A$	s ⁻¹
Second-order, $n=2$	$-r_A = k_A (C_A)^2$	L/mol.s

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Elementary Reactions

□ Elementary Reaction:

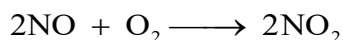
An *elementary reaction* is one that involves a single step reaction, such as the bimolecular rxn between oxygen free radical and methanol:



- The stoichiometric coefficients in this rxn are identical to the powers in the rate law: $-r_A = k(C_{\text{O}\cdot})(C_{\text{CH}_3\text{OH}})$
- Therefore, we say both the rxn and the rate law are elementary.
- This form of the rate law can be derived from Collision Theory (Professional Reference Shelf 3A on the CD-ROM).

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Elementary Reactions



$$-r_A = k_{\text{NO}} C_{\text{NO}}^2 C_{\text{O}_2}$$

- There are many rxns where the stoichiometric coefficients in the rxn are identical to the rxn orders but the rxns are not elementary!
- This is because these are not single step rxns, but involve series of rxns, i.e. there are rxn pathways involving active intermediates.
- For these rxns that are not elementary but whose stoichiometric coefficients are identical to the rxn orders in the rate law, we say the reaction **follows an elementary rate law**.
- For example, the oxidation reaction: $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ is not elementary but follows the elementary rate law:

$$-r_A = k_{\text{NO}} C_{\text{NO}}^2 C_{\text{O}_2}$$

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Following an elementary rate law

- In summary, for many rxns involving multiple steps and pathways, the powers in the rate laws surprisingly agree with the stoichiometric coefficients.
- For these rxns, we say that they follow elementary rate laws.

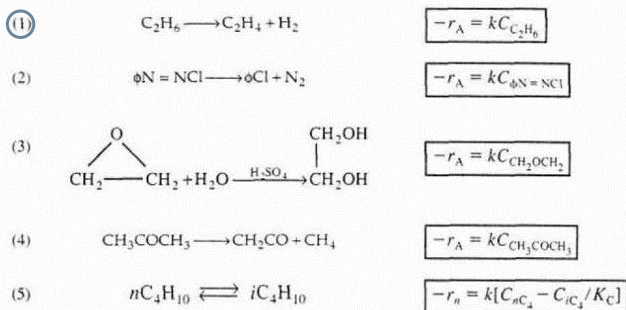
Please note that rate laws:

- are determined by experimental observation!
- are function of the rxn chemistry and not the type of reactor in which the reactions occur.

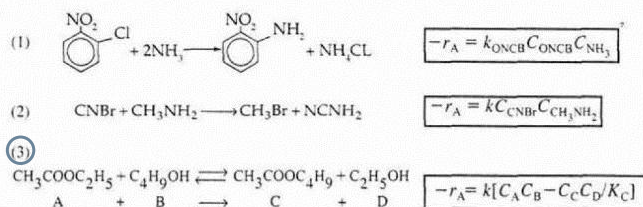
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TABLE 2-1. EXAMPLES OF REACTION RATE LAWS

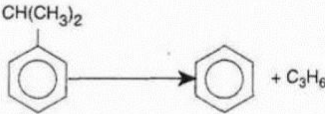
A. First-Order Rate Laws



B. Second-Order Rate Laws

* See Problem P3-13_B and Section 9.2.

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TABLE 3-1. EXAMPLES OF REACTION RATE LAWS (CONTINUED)	
C. Nonelementary Rate Laws	
① $\text{CH}_3\text{CHO} \longrightarrow \text{CH}_4 + \text{CO}$	$-r_{\text{CH}_3\text{CHO}} = kC_{\text{CH}_3\text{CHO}}^{3/2}$
(2)  Cumene (C) $\longrightarrow$ Benzene (B) + Propylene (P)	$-r_C = \frac{k[(P_C - P_B P_P)K_P]}{1 + K_B P_B + K_C P_C}$
D. Enzymatic Reactions (Urea (U) + Urease (E))	
$\text{NH}_2\text{CONH}_2 + \text{Urease} \xrightarrow{+\text{H}_2\text{O}} 2\text{NH}_3 + \text{CO}_2 + \text{Urease}$	$-r_U = \frac{kC_U}{K_M + C_U}$
E. Biomass Reactions	
Substrate (S) + Cells (C) $\longrightarrow$ More Cells + Product	$-r_U = \frac{kC_S C_C}{K_S + C_S}$
<i>Note:</i> The rate constant, k , and activation energies for a number of the reactions in these examples are given in the Data Base on the CD-ROM and Summary Notes.	

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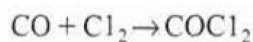
3.2.2 Nonelementary Rate Laws

- A large number of both homogeneous and heterogeneous rxns do not follow simple elementary rate laws.

- Examples are:

A) Homogeneous Reactions

- The order of rxn wrt any individual component does not have to be an integer.
- e.g., consider the gas-phase synthesis of phosgene:



in which the kinetic rate law is:

$$-r_{\text{CO}} = kC_{\text{CO}}C_{\text{Cl}_2}^{3/2}$$

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A) Homogeneous Reactions

- Sometimes reactions have complex rate expressions that cannot be separated into solely T -dependent & C_i -dependent portions.
- e.g., consider decomposition of nitrous oxide: $2\text{N}_2\text{O} \rightarrow 2\text{N}_2 + \text{O}_2$
in which the kinetic rate law is:
$$-r_{\text{N}_2\text{O}} = \frac{k_{\text{N}_2\text{O}} C_{\text{N}_2\text{O}}}{1 + k' C_{\text{O}_2}}$$
- Here we can only speak of **apparent reaction orders** under certain limiting conditions.
- Rate expressions of this type are very common for liquid & gaseous reactions promoted by solid catalysts (Chap. 10) and homogeneous rxn systems with reactive intermediates (Chap. 7).
- Chap. 7 discusses rxn mechanisms and pathways that lead to nonelementary rate laws.

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3.2.2 Nonelementary Rate Laws

B) Heterogeneous Reactions

- In many gas-solid catalyzed rxns, the rate law is commonly written in terms of partial pressures rather than concentrations.
- An example of a heterogeneous rxn is the hydrodemethylation of toluene (T) to form benzene (B) & methane (M) carried out over a solid catalyst: $\text{C}_6\text{H}_5\text{CH}_3 + \text{H}_2 \xrightarrow{\text{cat}} \text{C}_6\text{H}_6 + \text{CH}_4$
- The $-r'_T$ follows Langmuir-Hinshelwood kinetics (Chap.10), & the rate law was found experimentally to be:
$$-r'_T = \frac{k P_{\text{H}_2} P_{\text{T}}}{1 + K_{\text{B}} P_{\text{B}} + K_{\text{T}} P_{\text{T}}}$$

where K_{B} & K_{T} are adsorption constants and k is the rate constant.

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B) Heterogeneous Reactions

- To express the rate of rxn in terms of concentration rather than partial pressure, we simply substitute for P_i using the ideal gas law:

$$P_i = C_i RT$$

- The rate of rxn per unit weight catalyst, $-r'_A$, and the rate of rxn per unit volume, $-r_A$, are related through the bulk density ρ_b (mass of solid/volume) of the catalyst particles in the fluid media:

$$-r_A = \rho_b (-r'_A)$$

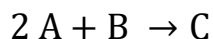
In summary on reaction orders:

- they **cannot** be deduced from rxn stoichiometry.
- Even though a number of rxns follow elementary rate laws, at least as many rxns do not.
- One **must** determine the rxn order from the literature or from experiments.

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Exercise

The following is a reaction that follows an elementary rate law, where A is a precious compound and used in limited quantities:



The rate law is written as:

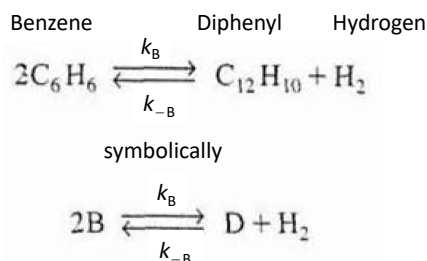
1. $-r_A = k_A C_A^2 C_B$
2. $-r_A = k_A C_A C_B^{1/2}$
3. $-r_A = k_A C_A^4 C_B^2$
4. All of the above are correct

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3.2.3 Reversible Reactions



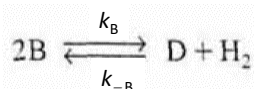
- To illustrate how to write rate laws for reversible reactions, we will use the following rxn:



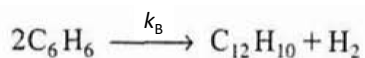
- In this discussion, we shall consider this gas-phase rxn to be elementary & reversible.

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3.2.3 Reversible Reactions



- The forward and reverse rate constants, k_B , and k_{-B} , respectively, are defined with respect to benzene.
- Benzene (B) is being depleted by the forward reaction:



in which the rate of disappearance of benzene is

$$-r_{\text{B,forward}} = k_B C_B^2$$

or the rate of formation of B for the forward rxn is

$$r_{\text{B,forward}} = -k_B C_B^2$$

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$2C_6H_6 \xrightarrow{k_B} C_{12}H_{10} + H_2$

$r_{B,forward} = -k_B C_B^2$

$2B \xrightleftharpoons[k_{-B}]{k_B} D + H_2$

□ For the reverse reaction between diphenyl (D) and hydrogen (H₂),

$$C_{12}H_{10} + H_2 \xrightarrow{k_{-B}} 2C_6H_6$$

the rate of formation of benzene is given as

$$r_{B,reverse} = k_{-B} C_D C_{H_2}$$

□ Again, both the rate constants k_B & k_{-B} are defined wrt benzene!!

□ The net rate of formation of benzene is the sum of the rates of formation from the forward rxn & the reverse rxn:

$$r_B \equiv r_{B,net} = r_{B,forward} + r_{B,reverse}$$

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$r_{B,forward} = -k_B C_B^2$

$r_{B,reverse} = k_{-B} C_D C_{H_2}$

$2B \xrightleftharpoons[k_{-B}]{k_B} D + H_2$

$$r_B \equiv r_{B,net} = r_{B,forward} + r_{B,reverse}$$

$$r_B = -k_B C_B^2 + k_{-B} C_D C_{H_2}$$

□ Or the rate of disappearance of Benzene, $-r_B$, is:

$$-r_B = k_B C_B^2 - k_{-B} C_D C_{H_2} = k_B \left(C_B^2 - \frac{k_{-B}}{k_B} C_D C_{H_2} \right)$$

□ At equilibrium, the net rate of formation of Benzene is **zero**, therefore

$$\frac{k_B}{k_{-B}} = \frac{C_{De} C_{H_2e}}{C_{Be}^2} \quad \text{From thermodynamics:} \quad \frac{C_{De} C_{H_2e}}{C_{Be}^2} = K_c$$

$$\therefore \frac{k_B}{k_{-B}} = K_c \quad \text{or} \quad \frac{k_{-B}}{k_B} = \frac{1}{K_c}$$

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$$-r_B = k_B \left(C_B^2 - \frac{k_{-B}}{k_B} C_D C_{H_2} \right) \quad \frac{k_{-B}}{k_B} = \frac{1}{K_c} \quad \frac{C_{De} C_{H_2e}}{C_{Be}^2} = K_c$$

$$\therefore -r_B = k_B \left(C_B^2 - \frac{C_D C_{H_2}}{K_c} \right)$$

Rate Law for the Reversible Reaction

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$$-r_B = k_B \left(C_B^2 - \frac{C_D C_{H_2}}{K_c} \right)$$

$$K_c = \frac{C_{De} C_{H_2e}}{C_{Be}^2}$$

□ Where do we get the values of the following constants?

□ k_B

□ K_c

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$$-r_B = k_B \left(C_B^2 - \frac{C_D C_{H_2}}{K_c} \right)$$

$$K_c = \frac{C_{De} C_{H_2e}}{C_{Be}^2}$$

- Where do we get the values of the following constants?
 - ▣ k_B ← Kinetics, rate constant (e.g., Arrhenius equation)
 - ▣ K_c ← Thermodynamics (e.g., $\ln K$ vs. $1/T$ figure or the equation $K(T) \equiv \exp\left(\frac{-\Delta G_{\text{rxn}}^0(T)}{RT}\right)$ where K is the **equilibrium constant**, which is function of T ONLY.

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A Review of Chemical Reaction Equilibria

Reversible Reactions

K , K_p & K_c

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3.2.3 Reversible Reactions

- Before we proceed, let's review some thermodynamics since we will be dealing a lot with reversible, equilibrium reactions.

- For the rxn $2A \leftrightarrow B$ (1),

$$K_{c1} = \frac{C_{Be}}{C_{Ae}^2} \quad \& \quad \Delta H^\circ_{rxn1} = \Delta H^\circ_{f,B} - 2 \Delta H^\circ_{f,A} \quad [J], [J/2 \text{ mol } A], \text{ or } [J/\text{mol } B]$$

- While if the same rxn is written as $A \leftrightarrow \frac{1}{2} B$ (2), then

$$K_{c2} = \frac{C_{Be}^{0.5}}{C_{Ae}} \quad \& \quad \Delta H^\circ_{rxn2} = 0.5 \Delta H^\circ_{f,B} - \Delta H^\circ_{f,A} \quad [J] \text{ or } [J/\text{mol } A]$$

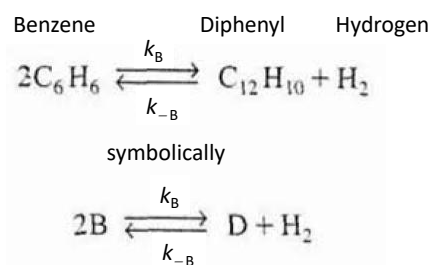
- Where $K_{c1} = (K_{c2})^2$ & $\Delta H^\circ_{rxn1} = 2 \times \Delta H^\circ_{rxn2}$

- $\therefore$ For thermodynamics calculations, rxns are considered as written

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3.2.3 Reversible Reactions

- Consider the following reaction:



- In this discussion, we shall consider this gas-phase rxn to be elementary & reversible.

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$$2\text{B} \xrightleftharpoons[k_{-B}]{k_B} \text{D} + \text{H}_2$$

□ For the benzene rxn, $K_c = \frac{C_{\text{De}} C_{\text{H}_2\text{e}}}{C_{\text{Be}}^2}$

where K_c represents the **Concentration Equilibrium Constant**.

□ What is **Equilibrium Constant** to begin with?

□ Remember the criterion of chemical-reaction equilibrium? $\sum_i \nu_i \mu_i = 0$

□ From this criterion, the following equation is derived:

$$\prod_i (\hat{f}_i / f_i^\circ)^{\nu_i} = \exp\left(\frac{-\Delta G^\circ(T)}{RT}\right)$$

where $\hat{f}_i$ is the fugacity of species i in solution/mixture
and f_i° is the standard state fugacity of species i .

What are the conditions of standard state?

Standard-State at given T : 1 bar, pure species, specified physical state.

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Ref: Wikipedia.org,
Smith & Van Ness

Could you please remind us what fugacity is?

In chemical thermodynamics, the **fugacity** (f_i) of a real gas is the corrected pressure (**effective pressure**) which replaces the actual (mechanical) pressure in accurate *chemical equilibrium* calculations.

For example, N_2 at 0°C and a pressure of 100 atm has a fugacity of 97 atm.

The fugacity coefficient (for pure gases) is defined as: $\phi_i \equiv f_i / P$

So what is ϕ_{N_2} at 0°C & 100 atm? The ϕ_{N_2} is just 0.97 with no units.

Steam at 300°C & 4,000 kPa has a fugacity of 3,611 kPa and, therefore, a fugacity coefficient of 0.903.

While steam at 300°C & 1 kPa has a fugacity of 1 kPa and, therefore, a fugacity coefficient of 1.0 (ideal gas).

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If effective pressure is called fugacity, then what effective concentration is called?

The effective concentration is represented by a quantity called “activity” which is given the symbol (a).

In chemical thermodynamics, activity is a measure of the “effective conc.” of a species in a mixture.

That means that the species' chemical potential depends on its activity in a real solution in the same way that it would depend on its conc. in an ideal solution.

Can you please simplify the concept by drawing an analogy?

To paint a wall you would need labors.

The following is a table that shows the relationship between the number of labors and the time consumed to paint the wall.

No of Labors	Time, hours	Effective No of Manpower
1	8	1
2	4	2
4	2.5	3.2
8	1.6	5

Ref: Wikipedia.org,
Smith & Van Ness

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- The species' chemical potential (μ_i) depends on its activity in a real solution in the same way that it would depend on its conc. in an ideal solution.
- By convention, activity is treated as a dimensionless quantity, although its actual value depends on customary choices of standard state for the species.
- The difference between activity and other measures of composition (e.g. conc.) arises because molecules in non-ideal solutions interact with each other, either to attract or to repel each other.
- Activities should be used to define equilibrium constants but, in practice, concentrations are often used instead. The same is often true of equations for reaction rates.
- However, there are circumstances where the activity & conc. are significantly different and, as such, it is not valid to approximate with conc. where activities are required.

Ref: Wikipedia.org,
Smith & Van Ness

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Back to

$$\prod_i (\hat{f}_i / f_i^\circ)^{\nu_i} = \exp\left(\frac{-\Delta G^\circ(T)}{RT}\right)$$

The term $\exp\left(\frac{-\Delta G^\circ}{RT}\right)$ is given the symbol K , and is called the

equilibrium constant for the rxn, and is function of temperature **ONLY**:

$$K \equiv \exp\left(\frac{-\Delta G^\circ(T)}{RT}\right)$$

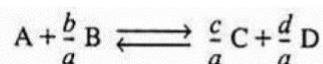
□ Therefore, $\prod_i (\hat{f}_i / f_i^\circ)^{\nu_i} = K \quad \because a_i \equiv \hat{f}_i / f_i^\circ$

$\therefore \prod_i (a_i)^{\nu_i} = K$, where a_i is the activity (effective concentration)

of species i & ν_i is its stoichiometric number.

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For the reaction:



1. The true (dimensionless) equilibrium constant

$$K = \frac{a_C^{c/a} a_D^{d/a}}{a_A a_B^{b/a}}$$

$$K = \prod_i (a_i)^{\nu_i}$$

K = True equilibrium constant
 K_p = Pressure equilibrium constant
 K_c = Concentration equilibrium constant

2. The pressure equilibrium constant K_p is

$$K_p = \frac{P_C^{c/a} P_D^{d/a}}{P_A P_B^{b/a}}$$

$$K_p = \prod_i (P_i)^{\nu_i}$$

3. The concentration equilibrium constant K_c is

$$K_c = \frac{C_C^{c/a} C_D^{d/a}}{C_A C_B^{b/a}}$$

$$K_c = \prod_i (C_i)^{\nu_i}$$

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$$K = \prod_i (a_i)^{\nu_i} \quad \text{where} \quad a_i = \hat{f}_i / f_i^0$$

(A) Equilibrium Constant (K) for Gas-Phase Reactions:

f_i^0 is the standard state fugacity.

The standard state for a gas is the ideal-gas state of the pure gas at the standard-state pressure P^0 of 1 bar.

Because the fugacity of an ideal gas is equal to its P , $f_i^0 = P^0 = 1 \text{ bar}$.

$\hat{f}_i$ is the fugacity of species i in the gas mixture.

The fugacity is related to the fugacity coefficient by: $\hat{\phi}_i = \hat{f}_i / P_i$

or $\hat{f}_i = \hat{\phi}_i P_i = \hat{\phi}_i y_i P$

Therefore, for gases: $a_i = \hat{f}_i / f_i^0 = \hat{\phi}_i P_i / P^0$

$$K = \prod_i (a_i)^{\nu_i} = \prod_i (\hat{\phi}_i P_i / P^0)^{\nu_i}$$

$$K = \prod_i (\hat{\phi}_i)^{\nu_i} \prod_i (P_i)^{\nu_i} \prod_i (P^0)^{-\nu_i}$$

$\hat{\phi}_i$ is a measure of deviation from ideal-gas (ig) behavior for gaseous mixtures:

$$\hat{\phi}_i \equiv \hat{f}_i / P_i$$

$$\hat{\phi}_i = \hat{f}_i / \hat{f}_i^{\text{ig}}$$

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$$K = \prod_i (a_i)^{\nu_i} \quad \text{where} \quad a_i = \hat{f}_i / f_i^0$$

(A) Equilibrium Constant (K) for Gas-Phase Reactions:

$$K = \prod_i (\hat{\phi}_i)^{\nu_i} \prod_i (P_i)^{\nu_i} \prod_i (P^0)^{-\nu_i}$$

$$K = K_\phi \cdot K_p \cdot (P^0)^{-\delta}$$

For ideal gases (high T , low P):

$$1. \quad \hat{\phi}_i = 1 \quad \therefore K_\phi = 1 \quad \& \quad K = K_p \cdot (P^0)^{-\delta}$$

$$2. \quad P_i = C_i RT$$

$$\therefore K_p = \prod_i (C_i RT)^{\nu_i} = (RT)^\delta \cdot \prod_i (C_i)^{\nu_i}$$

$$K_p = (RT)^\delta \cdot K_c \quad \Leftrightarrow \quad K = K_c \cdot (RT / P^0)^\delta$$

where,

$$K_\phi \equiv \prod_i (\hat{\phi}_i)^{\nu_i}$$

$$K_p \equiv \prod_i (P_i)^{\nu_i}$$

$$\delta \equiv \sum_i \nu_i$$

where,

$$K_c \equiv \prod_i (C_i)^{\nu_i}$$

For reactions between ideal gases with no change in the total number of moles ($\delta=0$): $K = K_p = K_c$

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$$K = \prod_i (a_i)^{\nu_i} \quad \text{where} \quad a_i = \hat{f}_i / f_i^0$$

(B) Equilibrium Constant (K) for Liquid-Phase Reactions:

f_i^0 is the standard state fugacity.

For liquids, f_i^0 is the fugacity of pure liquid i at the system T and 1 bar.

$\hat{f}_i$ is the fugacity of species i in the solution.

The fugacity is related to the activity coefficient by: $\hat{f}_i = \gamma_i x_i f_i$

where f_i is fugacity of pure liquid i at system T & P .

Therefore, for liquid solution:

$$a_i = \hat{f}_i / f_i^0 = \gamma_i x_i f_i / f_i^0 = \gamma_i x_i (f_i / f_i^0)$$

Because the fugacities of liquids are weak functions of P , the ratio f_i / f_i^0 is often taken as unity.

$$\therefore a_i = \hat{f}_i / f_i^0 \cong \gamma_i x_i$$

γ_i is a measure of deviation from ideal-solution (id) behavior for liquid solutions:

$$\gamma_i \equiv \hat{f}_i / x_i f_i$$

$$\gamma_i = \hat{f}_i / \hat{f}_i^{id}$$

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$$K = \prod_i (a_i)^{\nu_i} \quad \text{where} \quad a_i = \hat{f}_i / f_i^0 = \gamma_i x_i$$

(B) Equilibrium Constant (K) for Liquid-Phase Reactions:

$$K = \prod_i (\gamma_i x_i)^{\nu_i} = \prod_i (\gamma_i)^{\nu_i} \prod_i (x_i)^{\nu_i} = K_\gamma \cdot K_x$$

$$K = \prod_i (\gamma_i x_i)^{\nu_i} = \prod_i (\gamma_i C_i / C_T)^{\nu_i}$$

$$K = \prod_i (\gamma_i)^{\nu_i} \prod_i (C_i)^{\nu_i} \prod_i (C_T)^{-\nu_i}$$

$$K = K_\gamma \cdot K_c \cdot (C_T)^{-\delta}$$

where,

$$K_\gamma \equiv \prod_i (\gamma_i)^{\nu_i}$$

$$K_c \equiv \prod_i (C_i)^{\nu_i}$$

$$K_x \equiv \prod_i (x_i)^{\nu_i}$$

For ideal solutions (molecular species are similar in size & chemical nature): $\gamma_i = 1$ $\therefore K_\gamma = 1$

$$K = K_c \cdot (C_T)^{-\delta}$$

where C_T (total conc. at equil.) = $N_T / V = (N_{T0} + \delta N_{A0} \text{Xe}) / V_0 = (C_{T0} + C_{A0} \delta \text{Xe})$

For reactions occurring in ideal solution with no change in the total number of moles ($\delta=0$): $K = K_c$

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$$K = \prod_i (a_i)^{\nu_i} \quad \text{where} \quad a_i = \hat{f}_i / f_i^\circ$$

In Summary:

1. For Gas Phase RXNs: $K = K_\phi \cdot K_p \cdot (P^\circ)^{-\delta}$

For ideal gases:

$$K = K_p \cdot (P^\circ)^{-\delta}$$

$$K = K_c \cdot (RT / P^\circ)^\delta$$

where,

$$K_\phi = \prod_i (\hat{\phi}_i)^{\nu_i}$$

$$K_p = \prod_i (P_i)^{\nu_i}$$

$$K_c = \prod_i (C_i)^{\nu_i}$$

$$\delta = \sum_i \nu_i$$

2. For Liquid Phase RXNs: $K = K_\gamma \cdot K_c \cdot (C_T)^{-\delta}$

For ideal solutions:

$$K = K_c \cdot (C_T)^{-\delta}$$

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The effect of Temperature on the Equilibrium Constant:

□ Recall Van't Hoff's equation: $\frac{d \ln K}{dT} = \frac{\Delta H_{rxn}^\circ(T)}{RT^2}$

□ If heat capacities, C_p , can be assumed constant or its average values can be used, ΔH_{rxn} can be written as:

$$\Delta H_{rxn}^\circ(T) = \Delta H_{rxn}^\circ(T_R) + \Delta C_p^\circ(T - T_R)$$

$$\therefore \frac{d \ln K}{dT} = \frac{\Delta H_{rxn}^\circ(T_R) + \Delta C_p^\circ(T - T_R)}{RT^2}$$

□ Upon integration:

$$\ln \frac{K(T_2)}{K(T_1)} = -\frac{\Delta H_{rxn}^\circ(T_R) - T_R \Delta C_p}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) + \frac{\Delta C_p}{R} \ln \left(\frac{T_2}{T_1} \right)$$

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The effect of Temperature on the Equilibrium Constant:

- Back to Van't Hoff's equation:

$$\frac{d \ln K}{dT} = \frac{\Delta H_{rxn}^{\circ}(T)}{RT^2}$$

- If ΔH° , the standard heat of rxn, is assumed independent of T (reasonable assumption over small T range), integration of the above Eq. leads:

$$\ln \frac{K(T_2)}{K(T_1)} = -\frac{\Delta H_{rxn}^{\circ}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

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Special Case 1: Ideal Gas with Constant ΔH_{rxn} :

$$\ln \frac{K(T_2)}{K(T_1)} = -\frac{\Delta H_{rxn}^{\circ}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

- For ideal gases: $\frac{K(T_2)}{K(T_1)} = \frac{K_p(T_2) \cdot (P^{\circ})^{-\delta}}{K_p(T_1) \cdot (P^{\circ})^{-\delta}} = \frac{K_p(T_2)}{K_p(T_1)}$

- Therefore, for ideal gas reaction mixture with constant ΔH_{rxn} :

$$K_p(T_2) = K_p(T_1) \exp \left[\frac{-\Delta H_{rxn}^{\circ}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

- and when there is no change in the total number of moles ($\delta=0$), $K = K_p = K_c$:

$$K_c(T_2) = K_c(T_1) \exp \left[\frac{-\Delta H_{rxn}^{\circ}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

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Special Case 2: Ideal Liquid Solution with Constant ΔH_{rxn} & $\delta = 0$

$$\ln \frac{K(T_2)}{K(T_1)} = -\frac{\Delta H_{rxn}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

- For ideal liquid solutions:

$$K = K_\gamma \cdot K_c \cdot (C_T)^{-\delta} \Rightarrow K = K_c \cdot (C_T)^{-\delta}$$

- For cases where $\delta = 0$, $K = K_c$
 □ Therefore, for ideal liquid solutions with constant ΔH_{rxn} & $\delta = 0$:

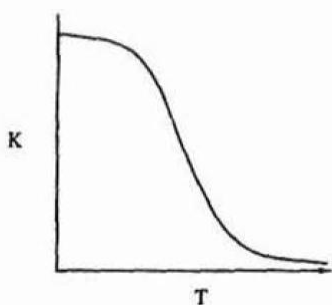
$$\ln \frac{K_c(T_2)}{K_c(T_1)} = -\frac{\Delta H_{rxn}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$K_c(T_2) = K_c(T_1) \exp \left[\frac{-\Delta H_{rxn}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

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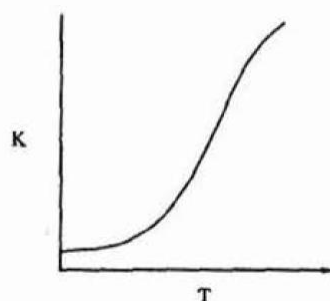
Quick test:

- Classify these rxns into exothermic or endothermic:



Reaction 1

Exothermic



Reaction 2

Endothermic

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The following conclusions may be drawn from thermodynamics:

1. If you have the value of the thermodynamic equilibrium constant (K), you can calculate the value of the concentration equilibrium constant (K_c).
2. K is unaffected by the P of the system, by the presence or absence of inerts, or by the kinetics of the rxn, but is affected by the T of the system.
3. i.e. $K = f(T)$ only & its value for a given rxn can be found by thermodynamic calculations or from thermodynamic charts.
4. Though K is unaffected by P or inerts, the equilibrium concentrations & X_e can be influenced by these variables.
5. $K \gg 1$ indicates that: practically complete conversion may be possible & that the rxn can be considered to be irreversible.
6. $K \ll 1$ indicates that: reaction will not proceed to any appreciable extent.

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The following conclusions may be drawn from thermodynamics:

6. K_c decreases with increasing T for exothermic rxns and increases with increasing T for endothermic rxns.
7. The shift in equilibrium is directly function of only two variables:
 - i. Temperature
 - ii. Reactants/Products concentrations/partial pressures
8. For an increase in T , X_e rises for endothermic rxns and drops for exothermic rxns.
9. For an increase in P in gas phase rxns:

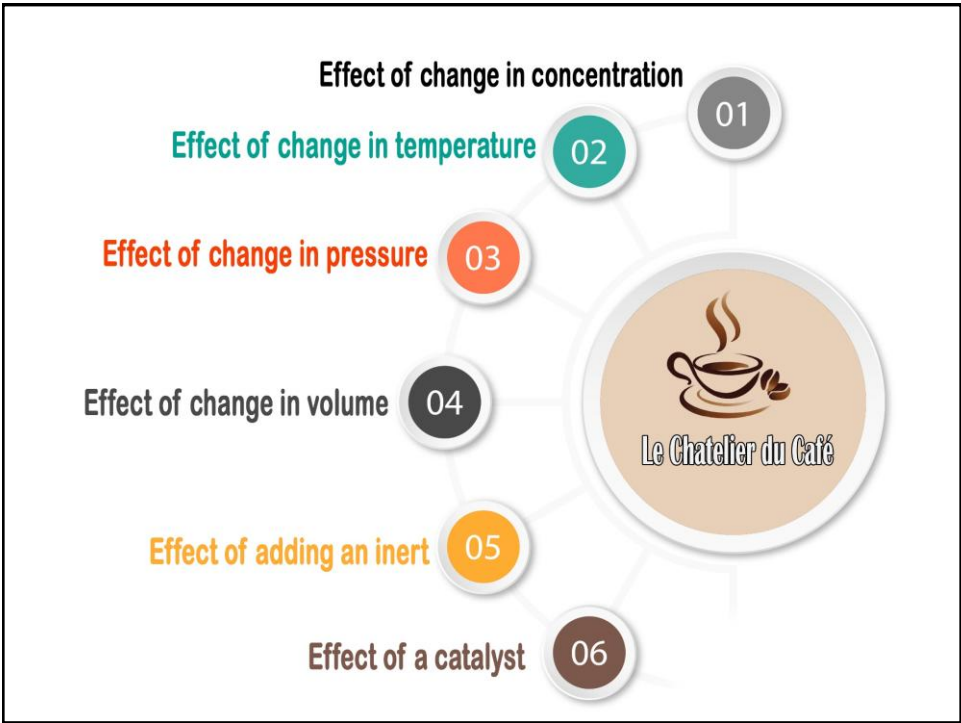
X_e rises when the no. of moles decreases with rxn (e.g. $2A \leftrightarrow B$) and X_e drops when the no. of moles increases with rxn (e.g. $A \leftrightarrow 2B$).
10. For an increase in inerts (dilution with variable V or v) for all rxns,

X_e drops when the no. of moles decreases with rxn (e.g. $2A \leftrightarrow B$) and X_e rises when the no. of moles increases with rxn (e.g. $A \leftrightarrow 2B$).

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The next 7 slides (2 pages) are from the following textbook and the authors' presentation:

Chapter 15: Chemical Equilibrium

Chemistry: The Molecular Nature of Matter, 6E

Jespersen/Brady/Hyslop

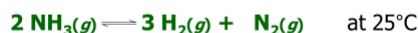


Ex. Manipulating Equilibria 1

1. When **direction** of equation is **reversed**, new **equilibrium constant** is **reciprocal** of original



$$K_c = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3[\text{N}_2]} = 4.26 \times 10^8$$



$$K'_c = \frac{[\text{H}_2]^3[\text{N}_2]}{[\text{NH}_3]^2} = \frac{1}{K_c} = \frac{1}{4.26 \times 10^8} = 2.35 \times 10^{-9}$$

Manipulating Equations for Chemical Equilibria

Various operations can be performed on equilibrium expressions

1. When **direction** of equation is **reversed**, new **equilibrium constant** is **reciprocal** of original



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Manipulating Equilibria 2

2. When coefficients in equation are **multiplied by a factor**, equilibrium constant is **raised to a power** equal to that factor.



$$K''_c = \frac{[\text{C}]^3[\text{D}]^3}{[\text{A}]^3[\text{B}]^3} = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]} \times \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]} \times \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]} = K_c^3$$

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Manipulating Equilibria 2

2. When coefficients in equation are **multiplied by factor**, equilibrium constant is **raised to power** equal to that factor



$$K_c = \frac{[\text{NH}_3]^2}{[\text{H}_2]^3[\text{N}_2]} = 4.26 \times 10^8$$

multiply by 3



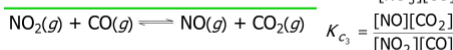
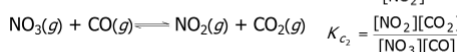
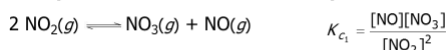
$$K''_c = \frac{[\text{NH}_3]^6}{[\text{H}_2]^9[\text{N}_2]^3} = K_c^3$$

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Manipulating Equilibria 3

3. When chemical **equilibria** are **added**, their **equilibrium constants** are **multiplied**



$$\frac{[\text{NO}][\text{NO}_3]}{[\text{NO}_2]^2} \times \frac{[\text{NO}_2][\text{CO}_2]}{[\text{NO}_3][\text{CO}]} = \frac{[\text{NO}][\text{CO}_2]}{[\text{NO}_2][\text{CO}]}$$

Therefore $K_{c_1} \times K_{c_2} = K_{c_3}$

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Manipulating Equilibria 3

3. When chemical **equilibria** are **added**, their **equilibrium constants** are **multiplied**



$$K_{c_3} = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]} \times \frac{[\text{F}][\text{G}]}{[\text{C}][\text{E}]} = \frac{[\text{D}][\text{F}][\text{G}]}{[\text{A}][\text{B}][\text{E}]} = K_{c_1} \times K_{c_2}$$

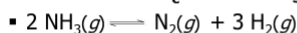
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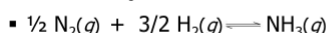
Learning Check

For: $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$
 $K_c = 500$ at a particular temperature.

What would be K_c for following?



$$K'_c = \frac{1}{K_c} = \frac{1}{500} = 0.002$$



$$K''_c = K_c^{1/2} = \sqrt{500} = 22.4$$

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Have you thought about these facts?!

- The stoichiometric number (ν_i) does not have a unit. It's not a ratio! it's totally unitless!!
- The extent of reaction (ξ or ε) is an extensive quantity that describes the rxn progress.
- It is calculated by dividing the number of moles generated of any species (G_i) in the rxn by its stoichiometric number: $\xi = G_i/\nu_i = (N_i - N_{i0})/\nu_i$
- The unit of ξ is mol (batch process) or mol/s (continuous process) and it's related to a given rxn but not to any specific species within the rxn.
- The Heat of Reaction (ΔH_{rxn}) is the amount of heat that must be added or removed during the rxn in order to keep all of the substances present at the same temperature.
- Its unit could be: kJ/mol reactant, kJ/mol product, or kJ/mol rxn, or kJ/mol extent of reaction!

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Insight into units of extent & heat of rxn: ξ & ΔH_{rxn}

The following example gives you an insight into the term moles of reaction or "mol" that is present in the units of the extent of rxn (ξ , mol or mol/s) and the enthalpy of rxn (ΔH_{rxn} , kJ/mol) for the reaction as written.

Example: In the rxn of interest, one molecule of A dissociates into two molecules of B. The enthalpy of rxn **for the stoichiometric equation, $A \rightarrow 2 B$** , is calculated from the enthalpies of formation as follows:

$$\Delta H_{rxn} = 2 \Delta H_{f,B} - \Delta H_{f,A} = 200 \text{ kJ, or kJ/mol A, or kJ/2 mol B, or kJ/mol of reaction, or kJ/mol of extent of reaction, or simply kJ/mol}$$

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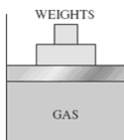
Example: In the rxn of interest, one molecule of A dissociates into two molecules of B. The rxn is to be carried out in a constant T & P batch reactor.

Calculate how much heat needs to be removed to run the rxn at constant T .

at t_0 :

$$N_{A0} = 1 \text{ mol}$$

$$N_{B0} = 0 \text{ mol}$$



at t_f :

$$N_A = 0.2 \text{ mol}$$

$$N_B = 1.6 \text{ mol}$$

Data:

$$X = 0.8$$

$$\Delta H_{rxn} = 200 \text{ kJ/mol A}$$

Solution 1: $A \rightarrow 2 B$

$$\Delta H_{rxn} = 200 \text{ kJ/mol A, or } 200 \text{ kJ/2 mol B, or } 200 \text{ kJ/mol}$$

kJ per mol of extent of rxn

$$\xi = -0.8/-1 = 0.8 \text{ mol}$$

moles of extent of rxn

$$Q = (N_{A0} - N_A) \cdot \Delta H_{rxn} = 0.8 \text{ mol A} \times 200 \text{ kJ/mol A} = 160 \text{ kJ, or}$$

$$Q = \xi \cdot \Delta H_{rxn} = 0.8 \text{ mol} \times 200 \text{ kJ/mol} = 160 \text{ kJ}$$

68

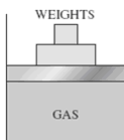
Example: In the rxn of interest, one molecule of A dissociates into two molecules of B. The rxn is to be carried out in a constant T & P batch reactor.

Calculate how much heat needs to be removed to run the rxn at constant T .

at t_0 :

$$N_{A0} = 1 \text{ mol}$$

$$N_{B0} = 0 \text{ mol}$$



at t_f :

$$N_A = 0.2 \text{ mol}$$

$$N_B = 1.6 \text{ mol}$$

Data:

$$X = 0.8$$

$$\Delta H_{rxn} = 200 \text{ kJ/mol A}$$

Solution 2: $\frac{1}{2} A \rightarrow B$

$$\Delta H_{rxn} = 100 \text{ kJ/mol B, or } 100 \text{ kJ/0.5 mol A, or } 100 \text{ kJ/mol}$$

$$\xi = -0.8/-0.5 = 1.6 \text{ mol}$$

$$Q = (N_{A0} - N_A) \cdot \Delta H_{rxn} = 0.8 \text{ mol A} \times 100 \text{ kJ/0.5 mol A} = 160 \text{ kJ, or}$$

$$Q = \xi \cdot \Delta H_{rxn} = 1.6 \text{ mol} \times 100 \text{ kJ/mol} = 160 \text{ kJ}$$

69

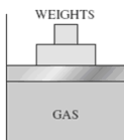
Example: In the rxn of interest, one molecule of A dissociates into two molecules of B. The rxn is to be carried out in a constant T & P batch reactor.

Calculate how much heat needs to be removed to run the rxn at constant T .

at t_0 :

$$N_{A0} = 1 \text{ mol}$$

$$N_{B0} = 0 \text{ mol}$$



at t_f :

$$N_A = 0.2 \text{ mol}$$

$$N_B = 1.6 \text{ mol}$$

Data:

$$X = 0.8$$

$$\Delta H_{rxn} = 200 \text{ kJ/mol A}$$

Solution 3: $2 A \rightarrow 4 B$

$$\Delta H_{rxn} = 400 \text{ kJ/2 mol A, or } 400 \text{ kJ/4 mol B, or } 400 \text{ kJ/mol}$$

$$\xi = -0.8 / -2 = 0.4 \text{ mol}$$

$$Q = (N_{A0} - N_A) \cdot \Delta H_{rxn} = 0.8 \text{ mol A} \times 400 \text{ kJ/2 mol A} = 160 \text{ kJ, or}$$

$$Q = \xi \cdot \Delta H_{rxn} = 0.4 \text{ mol} \times 400 \text{ kJ/mol} = 160 \text{ kJ}$$

70

Back to Chemical Reaction Engineering

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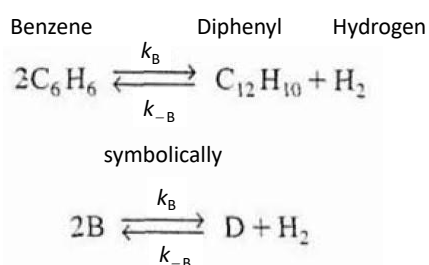
Lecture 12

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3.2.3 Reversible Reactions

- For the following elementary, reversible rxn:



the rate law was found to be:

$$\therefore -r_B = k_B \left(C_B^2 - \frac{C_D C_{H_2}}{K_c} \right)$$

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$$-r_B = k_B \left(C_B^2 - \frac{C_D C_{H_2}}{K_c} \right)$$

$$K_c = \frac{C_{De} C_{H_2e}}{C_{Be}^2}$$

□ Where do we get the values of the following constants?

▣ k_B

▣ K_c

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$$-r_B = k_B \left(C_B^2 - \frac{C_D C_{H_2}}{K_c} \right)$$

$$K_c = \frac{C_{De} C_{H_2e}}{C_{Be}^2}$$

□ Where do we get the values of the following constants?

▣ k_B ← Kinetics, rate constant (e.g., Arrhenius equation)

▣ K_c ← Thermodynamics (e.g., $\ln K$ vs. $1/T$ figure or the equation $K(T) \equiv \exp\left(\frac{-\Delta G_{rxn}^0(T)}{RT}\right)$ where K is the **equilibrium constant**, which is function of T ONLY.

□ Let's go to the **Thermodynamics World** to find the needed K_c .

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Find K_c needed from

Thermodynamics:

$$2B \overset{k_B}{\rightleftharpoons} D + H_2$$
$$k_{-B}$$
$$\ln K$$

□ For a given T , the following can be determined: $\ln K \rightarrow K \rightarrow K_c$

□ However, for the rxn $B \leftrightarrow \frac{1}{2} D + \frac{1}{2} H_2$, $(K_c)_{Fig} = \frac{C_{De}^{0.5} C_{H2e}^{0.5}}{C_{Be}}$ based on the stoichiometric numbers shown.

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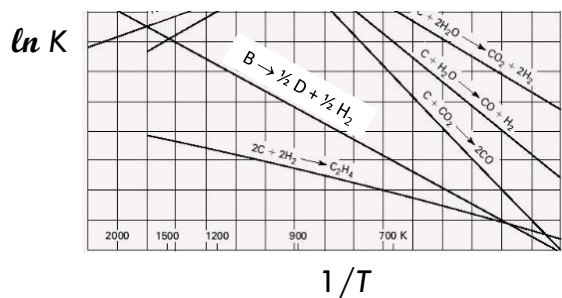
Thermodynamics:

□

□ However, for the rxn $B \leftrightarrow \frac{1}{2} D + \frac{1}{2} H_2$, $(K_c)_{Fig} = \frac{C_{De}^{0.5} C_{H2e}^{0.5}}{C_{Be}}$ based on the stoichiometric numbers shown.

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Thermodynamics:

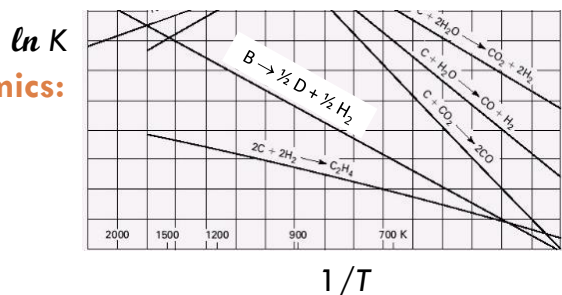


□

- However, for the rxn $B \leftrightarrow \frac{1}{2} D + \frac{1}{2} H_2$, $(K_c)_{Fig} = \frac{C_{De}^{0.5} C_{H2e}^{0.5}}{C_{Be}}$ based on the stoichiometric numbers shown.

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Thermodynamics:



- However, for the rxn $B \leftrightarrow \frac{1}{2} D + \frac{1}{2} H_2$, $(K_c)_{Fig} = \frac{C_{De}^{0.5} C_{H2e}^{0.5}}{C_{Be}}$ based on the stoichiometric numbers shown.

- While in the rate law of the rxn $2 B \leftrightarrow D + H_2$,

$$-r_B = k_B \left(C_B^2 - \frac{C_D C_{H_2}}{K_c} \right), K_c \text{ is expressed as } K_c = \frac{C_{De} C_{H_2e}}{C_{Be}^2}$$

- Therefore, K_c is calculated from $(K_c)_{Fig}$ through:

$$K_c = (K_c)_{Fig}^2$$

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Assume that $(K_c)_{Fig} = \frac{C_{De}^{0.5} C_{H_2e}^{0.5}}{C_{Be}}$ was found to be 2.

Knowing that $-r_B = k_B \left(C_B^2 - \frac{C_D C_{H_2}}{K_c} \right)$ and $K_c = \frac{C_{De} C_{H_2e}}{C_{Be}^2}$,

then $K_c = (K_c)_{Fig}^2 = 4$ $2 B \leftrightarrow D + H_2$

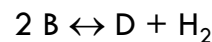
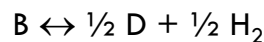
- From thermodynamics, where the reaction mixture is ideal gas, no change in total no. of moles ($\delta=0$), ΔH_{rxn} is constant, & $K_c(T_1) = 4$, $K_c(T)$ is found from:

$$K_c(T) = K_c(T_1) \exp \left[\frac{-\Delta H_{rxn}^o}{R} \left(\frac{1}{T} - \frac{1}{T_1} \right) \right]$$

- In the above equation, which ΔH_{rxn}^o is used?

1) $\Delta H_{rxn}^o = \frac{1}{2} \Delta H_{f,D}^o - \Delta H_{f,B}^o$

2) $\Delta H_{rxn}^o = \Delta H_{f,D}^o - 2 \Delta H_{f,B}^o$



80

Assume that $(K_c)_{Fig} = \frac{C_{De}^{0.5} C_{H_2e}^{0.5}}{C_{Be}}$ was found to be 2.

Knowing that $-r_B = k_B \left(C_B^2 - \frac{C_D C_{H_2}}{K_c} \right)$ and $K_c = \frac{C_{De} C_{H_2e}}{C_{Be}^2}$,

then $K_c = (K_c)_{Fig}^2 = 4$

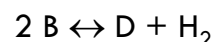
- From thermodynamics, where the reaction mixture is ideal gas, no change in total no. of moles ($\delta=0$), ΔH_{rxn} is constant, & $K_c(T_1) = 4$, $K_c(T)$ is found from:

$$K_c(T) = K_c(T_1) \exp \left[\frac{-\Delta H_{rxn}^o}{R} \left(\frac{1}{T} - \frac{1}{T_1} \right) \right]$$

- In the above equation, which ΔH_{rxn}^o is used?

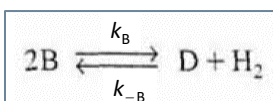
1) $\Delta H_{rxn}^o = \frac{1}{2} \Delta H_{f,D}^o - \Delta H_{f,B}^o$

2) $\Delta H_{rxn}^o = \Delta H_{f,D}^o - 2 \Delta H_{f,B}^o$



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□ Back to **Kinetics' World**



$$-r_B = k_B \left(C_B^2 - \frac{C_D C_{H_2}}{K_c} \right)$$

- Now, derive the rate of formation of diphenyl, r_D , in terms of the concentrations of H_2 , D, & B and k_D .
- The rate of formation of diphenyl, r_D , **must** have the same functional dependence on the reacting species concentrations as does the rate of disappearance of benzene, $-r_B$.

□ The rate of formation of diphenyl is:
$$r_D = k_D \left(C_B^2 - \frac{C_D C_{H_2}}{K_c} \right)$$

- Recall the established relationship between the rates of reaction:

$$\frac{r_B}{-2} = \frac{r_D}{1} = \frac{r_{H_2}}{1}$$

Do this @ home

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$$\frac{r_B}{-2} = \frac{r_D}{1} = \frac{r_{H_2}}{1}$$

$$-r_B = k_B \left(C_B^2 - \frac{C_D C_{H_2}}{K_c} \right)$$

$$r_D = k_D \left(C_B^2 - \frac{C_D C_{H_2}}{K_c} \right)$$

$$2\text{B} \xrightleftharpoons[k_{-B}]{k_B} \text{D} + \text{H}_2$$

$$\therefore \frac{-r_B}{2} = r_D$$

$$\therefore \frac{k_B}{2} \left(C_B^2 - \frac{C_D C_{H_2}}{K_c} \right) = k_D \left(C_B^2 - \frac{C_D C_{H_2}}{K_c} \right)$$

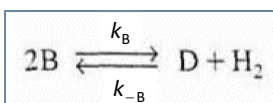
- Find the relationship between k_B & k_D .

$$\frac{k_B}{2} = k_D$$

- Or
$$\frac{k_B}{2} = \frac{k_D}{1} = \frac{k_{H_2}}{1}$$
- Consequently, we see the need to define the rate constant, k , wrt a particular species.

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□ Back to **Kinetics' World**



$$-r_B = k_B \left(C_B^2 - \frac{C_D C_{H_2}}{K_c} \right)$$

Final Remarks:

- At equilibrium, the rate of reaction is identically zero for all species.
- All rate laws for reversible rxns must reduce to the thermodynamic relationship relating the reacting species concentrations at equilibrium. [see Problem P3-2 (i)]
- Verify that for the above rate law.

$$-r_B = 0 = k_B \left(C_{Be}^2 - \frac{C_{De} C_{H_2e}}{K_c} \right)$$

$$K_c = \frac{C_{De} C_{H_2e}}{C_{Be}^2}$$

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Test yourself at Home! (will be needed for problem 4-9)



20 min

A reversible liquid-phase isomerization $A \rightleftharpoons B$ is carried out *isothermally* in a 1000-gal CSTR. The reaction is second order in both the forward and reverse directions. The reaction is reversible with $K_C = 3.0$ at 300 K, and $\Delta H_{Rx}^\circ = -25,000$ cal/mol.

$$K_C(T) = K_C(T_0) \exp \left[\frac{\Delta H_{Rx}^\circ}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right]$$

1. Derive the rate law for this non-elementary rxn.

2. What is the expression of K_c used in the rate law?

$\ln K$

3. What is the expression of the given K_c ?

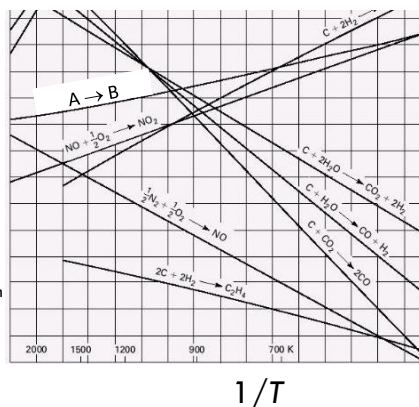
4. What is the relationship between K_c &

$(K_c)_{\text{given}}$?

5. What are the values of T_0 , $K_c(T_0)$, & $\Delta H_{\text{rxn}}^\circ$ that will be used in the K_c equation above?

6. Calculate the rate law K_c at 310K.

[Answer: 0.60]



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$$-r_B = k_B \left(C_B^2 - \frac{C_D C_{H_2}}{K_c} \right)$$



Q: Do I need to derive the rate law for reversible reactions in each problem they appear in?



A: NO!



However, you will need to derive the rate law if:

1. you were asked to
2. the rxn is not elementary
3. the available $K_c \neq$ the K_c in the rate law



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3.3 The Reaction Rate Constant



25 min

- The rxn rate constant k is not truly a constant: it is merely $k \neq f(C_i)$
- The quantity k is referred to as either the **specific reaction rate** or the **rate constant**.
- It is almost always strongly dependent on T .
- It depends on whether or not a catalyst is present.
- In gas-phase reactions, k may be a $f(P)$.
- In liquid systems, it can also be a $f(\text{ionic strength, solvent type})$.
- The last two variables (solvent type & P) normally exhibit much less effect on k than T does (with the exception of supercritical solvents).

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3.3 The Reaction Rate Constant

- This assumption is valid in most laboratory & industrial reactions, and seems to work quite well.
- It was the great Swedish chemist Arrhenius who first suggested that the T dependence of k_A could be correlated by:

$$k_A(T) = Ae^{-E/RT}$$

A = preexponential factor or frequency factor

E = activation energy, J/mol or cal/mol

R = gas constant = 8.314 J/mol · K = 1.987 cal/mol · K

T = absolute temperature, K

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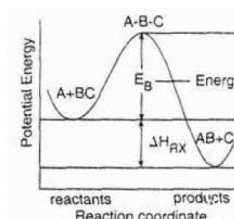
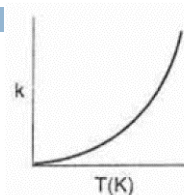
3.3 The Reaction Rate Constant

$$k_A(T) = Ae^{-E/RT}$$

- **Arrhenius Equation** has been verified empirically to give the T behavior of most rxn rate constants within experimental accuracy over fairly large T ranges.
- The Arrhenius Eq. is derived in the Collision Theory section on the CD-ROM.



- A is the pre-exponential factor or frequency factor.
- It is the decay rate to the products and is **function** of the *lifetime* of the activated species & the *likelihood* that it will convert to a product instead of back to a reactant.



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3.3 The Reaction Rate Constant

$$k_A(T) = Ae^{-E/RT}$$

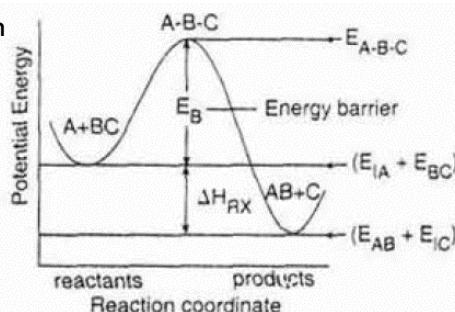
- Why is there an activation energy?
- If the reactants are free radicals that essentially react immediately on collision, there usually isn't an activation energy.
- However, for most atoms and molecules undergoing rxn, there is an activation energy.
- A couple of the reasons are that in order to react:
 1. The steric and electron repulsion forces must be overcome as the reacting molecules come close together.
 2. The molecules need energy to distort or stretch their bonds so that they break them before forming new bonds.

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3.3 The Reaction Rate Constant

$$k_A(T) = Ae^{-E/RT}$$

- The activation energy can be thought of as a barrier to energy transfer (from the kinetic energy to the potential energy) between reacting molecules that must be overcome.
- The term $e^{-E/RT}$ represents the fraction of collisions that have enough energy to overcome the activation barrier at temperature T .
- This fraction increases as the T increases. Why?
Is that reflected mathematically in the Arrhenius Eq.?



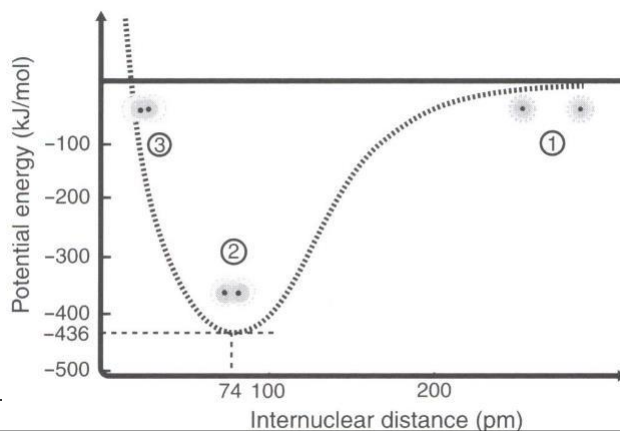
For more info, read the following slides at home

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Bonds and Energy

- When atoms come together, they form bonds, lowering their total energy.
- Energy is released when a bond is formed.
- Energy is absorbed when bond is broken.

Fig: Bonding energy versus internuclear separation for H-H bond.



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- One way to view the barrier to a rxn is through the use of the **reaction coordinates**.
- These coordinates denote the potential energy of the system as a function of the progress along the reaction path as we go from reactants to an intermediate to products.

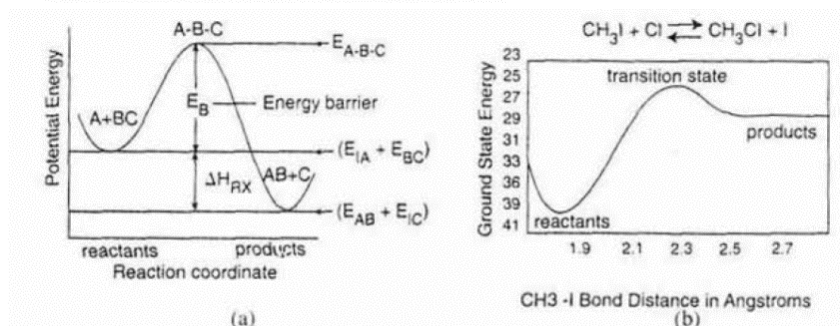
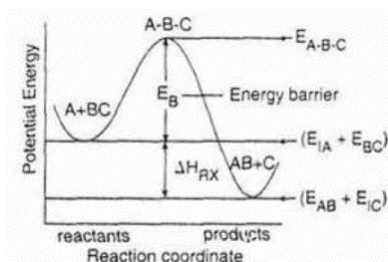


Figure 3-1 Progress along reaction path. (a) Symbolic reaction; (b) Calculated from computational software on the CD-ROM Chapter 3 Web Module.

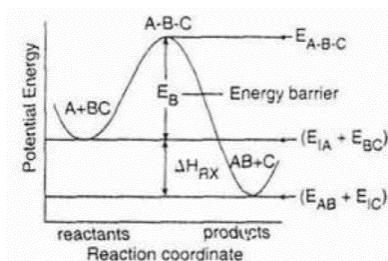
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- The figure shows the potential energy of the three atom (or molecule) system, A, B, & C, as well as the reaction progress as we go from reactant species A & BC to products AB and C.
- Initially A and BC are far apart & the system energy is just the bond energy BC.
- At the end of the rxn, the products AB and C are far apart, and the system energy is the bond energy AB.
- As we move along the reaction coordinate (x-axis) to the right, the reactants A and BC approach each other, the BC bond begins to break, & the energy of the rxn pair increases until the top of the barrier is reached.
- At the top, the **transition state** is reached where the intermolecular distance between AB and between BC are equal (i.e., A-B-C).
- As a result, the potential energy of the initial three atoms (molecules) is high.



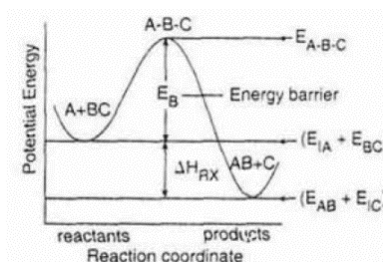
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- As the rxn proceeds further, the distance between A and B decreases, and the AB bond begins to form.
- As we proceed further, the distance between AB and C increases and the energy of the reacting pair decreases to that of the AB bond energy.
- The calculations to arrive at Figure 3-I(b) are discussed in the CD-ROM web module, and transition state theory is discussed in the CD-ROM Professional Reference Shelf R3.2 Transition State Theory.



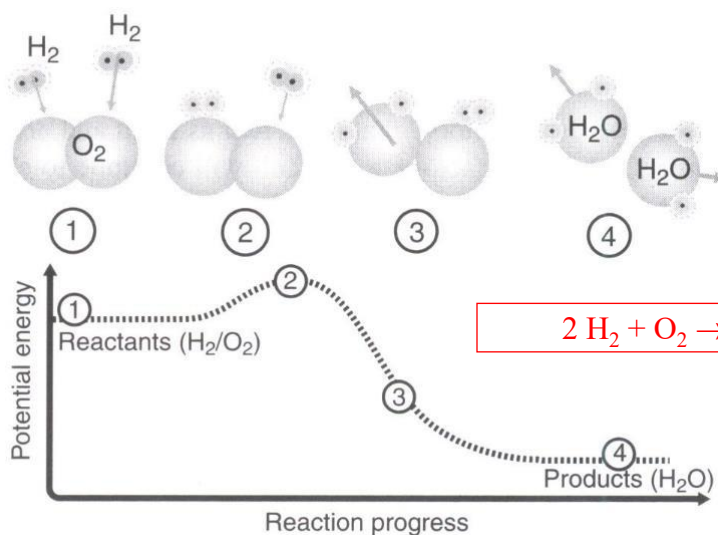
95

- We see that for the rxn to occur, the reactants must overcome an energy barrier, E_B , as shown in the Figure.
- The energy barrier, E_B , is related to the activation energy, E .
- E_B can be calculated from:
$$E_B = E_{fA-B-C}^{\circ} - (E_{fA}^{\circ} + E_{fB-C}^{\circ})$$
- The energy of formation, E_f , of the reactants can be found in the literature while the energy of formation of transition state can be calculated using a number of software programs such as CACHE, Spartan. or Cerius.
- The activation energy, E_a , is often approximated by the barrier height, which is a good approximation in the absence of quantum mechanical tunneling.



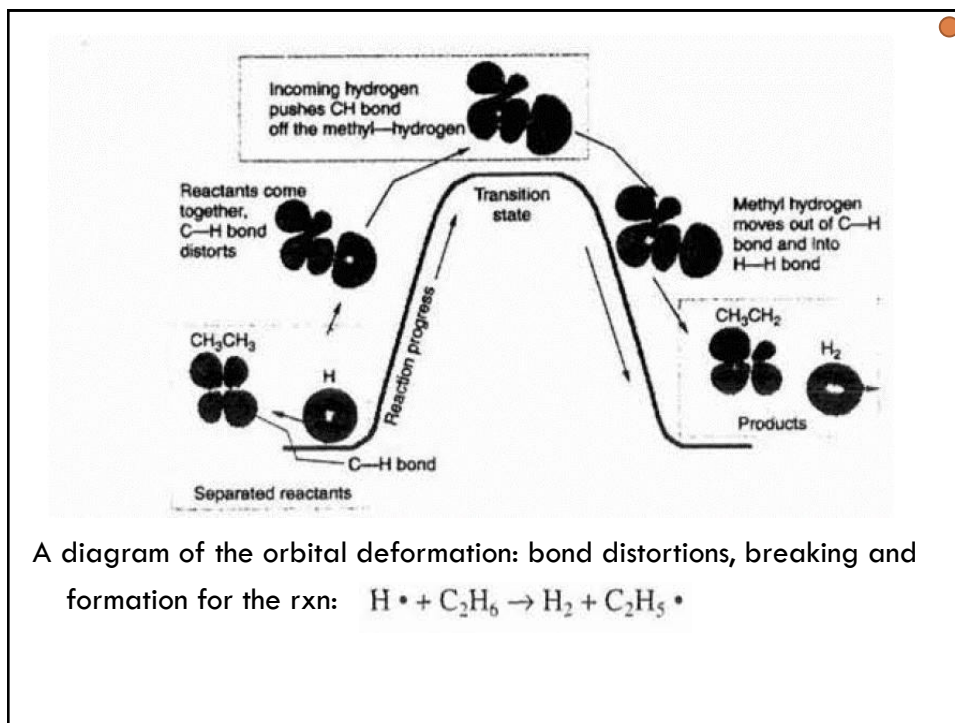
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Fig: Schematic of H_2 - O_2 combustion reaction. Arrows indicate the relative motion of the molecules participating in the rxn. Starting with the reactants H_2 & O_2 gases (1) H-H & O-O bonds must first be broken, requiring energy input (2) before H-O bonds are formed, leading to energy outputs (3,4).



Ref: O'Hayre, R. P.; Cha, S.; Colella, W.; Prinz, F. B. Fuel Cell Fundamentals; 1st ed. Wiley & Sons: New York, 2006.

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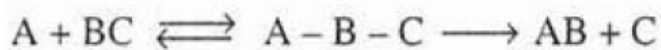
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Activation Energy Explained by Collision Theory

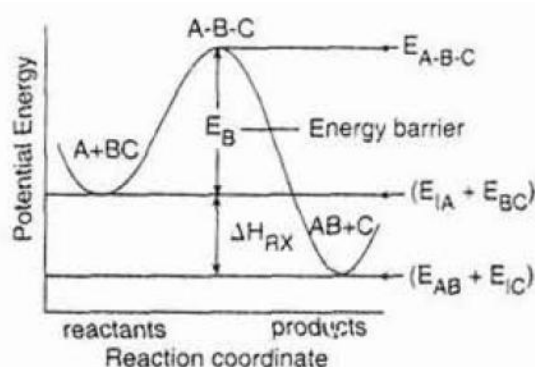
- By increasing T , the kinetic energy of the reactant molecules increases.
- Part of this kinetic energy will be in turn transferred through molecular collisions to internal energy.
- In turn this will increase the stretching and bending of the bonds, causing them to reach an activated state, vulnerable to bond breaking and reaction.

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Insight into the Rate Law



$$-r_A = A \cdot e^{-E/RT} \cdot C_A \cdot C_{BC}$$



100

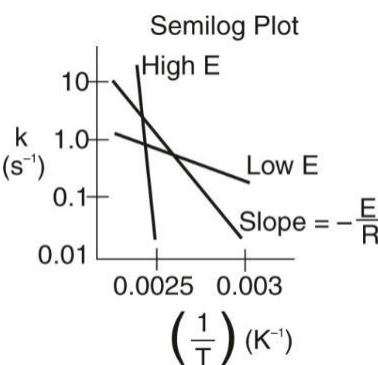
How is the activation energy determined?

$$k_A(T) = A e^{-E/RT}$$

- How is the activation energy, E , determined?

$$\ln k_A = \ln A - \frac{E}{R} \left(\frac{1}{T} \right)$$

- It is obtained experimentally by carrying out the rxn at several different T , then plotting $\ln k_A$ vs. $(1/T)$ and finding the slope.



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k as function of T

$$k_A(T) = Ae^{-E/RT}$$

- In literature, the value of k for specific rxn is reported at a specific T along with its E value.
- What if I need k at another T ?!
- Knowing the value of k_A at (T_1) , we can estimate k_A at (T_2) for that rxn, if E is known.
- How?

$$k_2 = k_1 e^{-\frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$

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Comments on the $k(T)$

$$k_A(T) = Ae^{-E/RT}$$

- The rate of rxn increases with the increase of T .
- Use the following eq. to calculate the ratio $k_2(310K)/k_1(300K)$ for different rxns (i.e. for different E): $k_2 = k_1 e^{-\frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$

rxn	E_a , kJ/mol	k_{310}/k_{300}
A + B → D	55	2.0
A + B → U	107	4.0
C → 2E	150	7.0
C + E → F	200	13.3

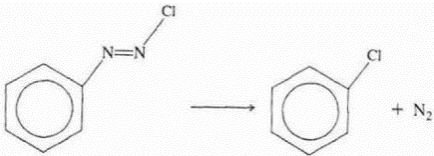
- The larger the E_a , the more temperature-sensitive is the rate of rxn.
- Why? (Answer me in the tutorial. Refer to the $f(E,T)$ vs E Fig. in Lecture 14)

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Determination of the Activation Energy

Example 3-1 (solve at home):

Calculate the activation energy for the decomposition of benzene diazonium chloride to give chlorobenzene and nitrogen, using the information in the given table for this first-order reaction:



$k \text{ (s}^{-1}\text{)}$	0.00043	0.00103	0.00180	0.00355	0.00717
$T \text{ (K)}$	313.0	319.0	323.0	328.0	333.0

$k_A(T) = Ae^{-E/RT}$

Solution:

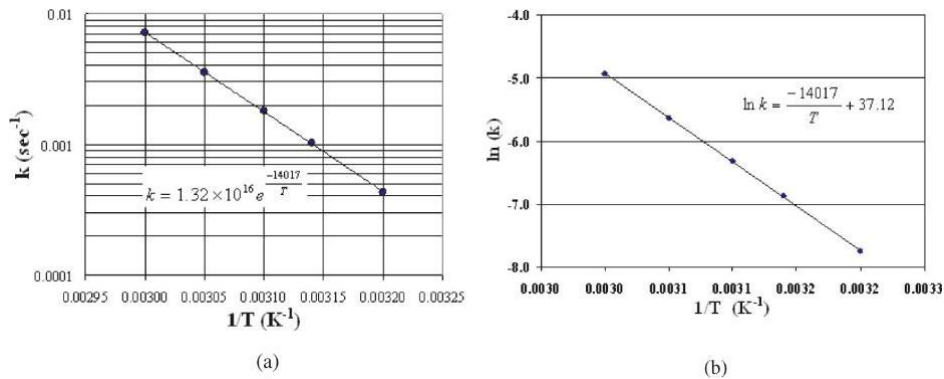
$\ln k_A = \ln A - \frac{E}{R}\left(\frac{1}{T}\right)$

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Solution of Example 3-1:

$k_A(T) = Ae^{-E/RT}$

$\ln k_A = \ln A - \frac{E}{R}\left(\frac{1}{T}\right)$



Answer: $E = 116.5 \frac{\text{kJ}}{\text{mol}}$ $A = 1.32 \times 10^{16} \text{ s}^{-1}$

105

Comments on Arrhenius Equations

$k_A(T) = Ae^{-E/RT}$

 45 min

- Postulation of the Arrhenius equation, remains the greatest single step in chemical kinetics, and retains its usefulness today, nearly a century later.
- While there are no typical values of A & E for a first-order gas-phase rxn, if one were forced to make a guess, values of A and E might be 10^{13} s^{-1} & 200 kJ/mol .
- However, for families of rxns (e.g., halogenation), a number of correlations can be used to estimate the activation energy.

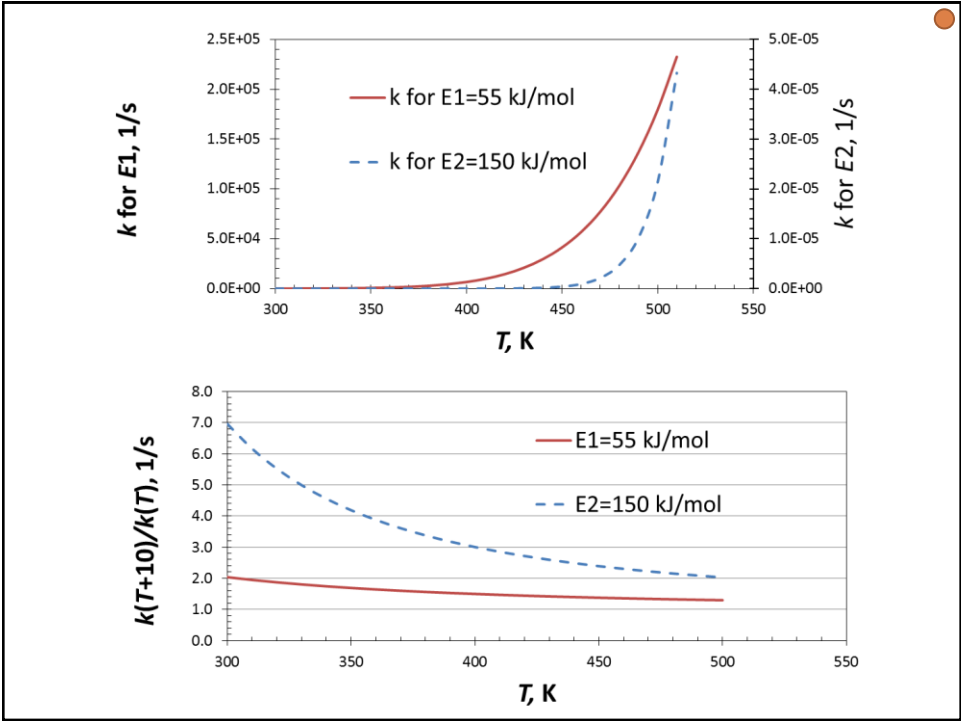
106

Comments on Arrhenius Equations

$k_A(T) = Ae^{-E/RT}$

- There is a rule of thumb that states that the rate of reaction doubles for every increase of 10°C in temperature.
- However, this is true only for a specific combination of E_a & T .
- For example, if $E_a = 55 \text{ kJ/mol}$, the rate will double only if T is raised from 300 K to 310 K .
- If the $E_a = 150 \text{ kJ/mol}$, the rule will be valid only if the T is raised from 500 K to 510 K .

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Complete Suggested Problems Set #3

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Lecture 13 – Week 4

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3.4 Present Status of Our Approach to Reactor Sizing and Design

- In Chap. 2, we showed how it was possible to size reactors using the design equations if $-r_A$ at different X are given.
- However, this kind of information is not unconditionally useful & $-r_A = f(X)$ is not directly available.
- However, we know that $-r_A = [k_A(T)][\text{fn}(C_A, C_B, \dots)]$ & $C_i = f(X)$, therefore, we can obtain $-r_A = f(X)$.
- So, if the rate law is given & the concentrations can be expressed as a function of X , then in fact we have $-r_A = f(X)$ and this is all that is needed to evaluate the design equations.

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3 Rate Laws and Stoichiometry

Part 2: Stoichiometry

Part 2: Stoichiometry

Prepared by: Dr Shaker Haji - CHENG 323

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Opening

- Now that we have shown how the rate law can be expressed as $f(C_i)$, we only need to express $C=f(X)$ in order to size reactors.
- If rate law depends on more than one species (e.g. $-r_A=f(C_A, C_B, C_C, C_D)$), we must relate the concentrations of the different species to each other.
- This relationship is easily established with the aid of a **stoichiometric table**.
- In formulating our stoichiometric table by using X, we shall take species A as our basis of calculation to put everything on a basis of “per mole of A”:



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Stoichiometric Table for a Batch Systems

$A + \frac{b}{a} B \longrightarrow \frac{c}{a} C + \frac{d}{a} D$

Species	Initially (mol)	Change (mol)	Remaining (mol)
A	N_{A0}	$N_A - N_{A0} = -N_{A0}X$	$N_A = N_{A0} - N_{A0}X$
B	N_{B0}	$-b/a N_{A0}X$	$N_B = N_{B0} - b/a N_{A0}X$
C	N_{C0}	$+c/a N_{A0}X$	$N_C = N_{C0} + c/a N_{A0}X$
D	N_{D0}	$+d/a N_{A0}X$	$N_D = N_{D0} + d/a N_{A0}X$
I (inert)	N_{I0}	<i>no change</i>	$N_I = N_{I0}$
Totals	N_{T0}		$N_T = N_{T0} + \delta N_{A0}X$

$\delta = \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right)$

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Stoichiometric Table for a Batch Systems

$A + \frac{b}{a} B \longrightarrow \frac{c}{a} C + \frac{d}{a} D$

Species	Initially (mol)	Change (mol)	Remaining (mol)
A	N_{A0}	$N_A - N_{A0} = -N_{A0}X$	$N_A = N_{A0} - N_{A0}X$
B	N_{B0}	$-b/a N_{A0}X$	$N_B = N_{B0} - b/a N_{A0}X$
C	N_{C0}	$+c/a N_{A0}X$	$N_C = N_{C0} + c/a N_{A0}X$

□ Write a general equation for $N_i(X)$.

$$N_i = N_{i0} + \nu_i N_{A0} X$$

□ N_{A0} may be taken as a common factor:

$$N_i = N_{A0} (N_{i0}/N_{A0} + \nu_i X)$$

□ If N_{i0}/N_{A0} is defined as θ_i then re-write $N_i(X)$.

$$N_i = N_{A0} (\theta_i + \nu_i X)$$

$$\Theta_i = \frac{N_{i0}}{N_{A0}} = \frac{C_{i0}}{C_{A0}} = \frac{y_{i0}}{y_{A0}}$$

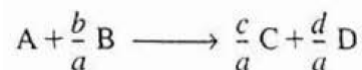
Where A is the limiting reactant

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CHENG 323

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3.5 Batch Systems



- Recall that the kinetic rate law (e.g., $-r_A = kC_A$) is a function solely of the intensive properties of the reacting system (e.g., T, P, C_i , & catalysts)
- Recall that $-r_A$ depends on C_i rather than N_i .
- Therefore, the calculated $N_i(X)$

$$N_i = N_{A0} (\theta_i + \nu_i X)$$

should be converted to $C_i(X)$ instead.

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3.5.1 Equations for Batch Concentrations

- The concentration of species i is the number of moles of i per unit volume:

$$C_i = \frac{N_i}{V}$$

- In general $C_i(X)$ can be written as

$$C_i(X) = \frac{N_i(X)}{V(X)}$$

- We know how to write $N_i(X)$: $N_i = N_{A0} (\theta_i + \nu_i X)$

Where A is the limiting reactant

- Now we need to learn how to find $V(X)$ to obtain $C_i(X)$.

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3.5.2 Constant-Volume Batch Reaction Systems

- Sometimes the reacting system undergoes no change in volume as the reaction progresses, $V \neq f(X)$.

$$C_i(X) = \frac{N_i(X)}{V(X)}$$

- These systems are called constant-volume or constant-density, because of the invariance of either volume or density during the reaction process.

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3.5.2 Constant-Volume Batch Reaction Systems

- This situation, where $V(X) = V = V_0$, may arise from several causes:

$$C_i(X) = \frac{N_i(X)}{V(X)}$$

1. Gas-phase rxn run in a sealed, constant-volume vessel
2. Liquid-phase rxns, where the rxn mixture is mainly solvent
3. No change in the total number of moles during isothermal & isobaric gas-phase rxns.

Example

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3.5.2 Constant-Volume Batch Reaction Systems

- In gas-phase batch systems, the reactor is usually a sealed constant-volume vessel with appropriate instruments to measure P & T within the reactor.
- The volume within this vessel is fixed and will not change ($V = V_0$).
- For liquid-phase reactions taking place in solution, the solvent usually dominates the situation.
- As a result, changes in the density of the solute **do not** affect the overall density of the solution significantly.
- Therefore, it is essentially a constant-volume reaction process.
- Most liquid-phase organic reactions do not change density during the rxn (can you think of an exception?)
- An important exception to this rule exists for polymerization processes.

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3.5.2 Constant-Volume Batch Reaction Systems

- Another example of a constant-volume gas-phase isothermal rxn occurs when the number of moles of products equals the number of moles of reactants.
- The water-gas shift reaction is one of these: $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$
- When the number of reactant molecules forms an equal number of product molecules at the same T & P , the volume of the reacting mixture will not change if the conditions are such that:
 - ▢ the ideal gas law is applicable, or if
 - ▢ the compressibility factors (Z) of the products and reactants are approximately equal.

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3.5.2 Constant-Volume Batch Reaction Systems

- For constant-volume systems, $C_i(X)$ equations can be simplified to:

$$\begin{aligned}
 V &= V_0 \\
 C_A &= \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X) \\
 C_B &= N_{A0} \frac{[(N_{B0}/N_{A0}) - (b/a)X]}{V_0} = \frac{N_{A0}[\Theta_B - (b/a)X]}{V_0} = C_{A0} \left(\Theta_B - \frac{b}{a}X \right) \\
 C_C &= N_{A0} \frac{[(N_{C0}/N_{A0}) + (c/a)X]}{V_0} = C_{A0} \left(\Theta_C + \frac{c}{a}X \right) \\
 C_D &= N_{A0} \frac{[(N_{D0}/N_{A0}) + (d/a)X]}{V_0} = C_{A0} \left(\Theta_D + \frac{d}{a}X \right) \\
 C_i &= C_{A0} (\Theta_i + \nu_i X)
 \end{aligned}$$

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3.5.2 Constant-Volume Batch Reaction Systems



25 min

Example

For the constant-volume rxn system, write the rate law, for the rxn:

$A + 2B \rightarrow C$, in terms of X . The reactants are charged at stoichiometric ratio and the rxn follows an elementary rate law.

125

3.5.2 Constant-Volume Batch Reaction Systems

Example

For the constant-volume rxn system, write the rate law, for the rxn:

$A + 2B \rightarrow C$, in terms of X . The reactants are charged at stoichiometric ratio and the rxn follows an elementary rate law.

$$-r_A = k_A \left[N_{A0} (1 - X) / V_0 \right] \left[N_{A0} (\Theta_B + \nu_B X) / V_0 \right]^2$$

$$-r_A = 4k_A C_{A0}^3 (1 - X)^3$$

- Substituting for the given parameters k , C_{A0} , & Θ_B , we can now use the techniques in Chap. 2 to size the CSTRs and PFRs for, e.g., liquid phase rxns.

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3.5.2 Constant-Volume Batch Reaction Systems

Example:

For the constant-volume rxn system discussed earlier: $A + 2B \rightarrow C$, calculate the concentrations of the involved species when $X = 0.8$ if the initial mixture consists of A at a concentration of 10 mol/L & B at a concentration of 25 mol/L.

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3.6 Flow Systems



40 min

Entering

F_{A0}
 F_{B0}
 F_{C0}
 F_{D0}
 F_{I0}

Leaving

F_A
 F_B
 F_C
 F_D
 F_I

$A + \frac{b}{a} B \longrightarrow \frac{c}{a} C + \frac{d}{a} D$

Figure 3-5 Flow reactor.

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TABLE 3-4. STOICHIOMETRIC TABLE FOR A FLOW SYSTEM

Species	Feed Rate to Reactor (mol/time)	Change within Reactor (mol/time)	Effluent Rate from Reactor (mol/time)
A	F_{A0}	$-F_{A0}X$	$F_A = F_{A0}(1 - X)$
B	$F_{B0} = \Theta_B F_{A0}$	$-\frac{b}{a} F_{A0}X$	$F_B = F_{A0} \left(\Theta_B - \frac{b}{a} X \right)$
C	$F_{C0} = \Theta_C F_{A0}$	$\frac{c}{a} F_{A0}X$	$F_C = F_{A0} \left(\Theta_C + \frac{c}{a} X \right)$
D	$F_{D0} = \Theta_D F_{A0}$	$\frac{d}{a} F_{A0}X$	$F_D = F_{A0} \left(\Theta_D + \frac{d}{a} X \right)$
I	$F_{I0} = \Theta_I F_{A0}$	—	$F_I = F_{A0} \Theta_I$
	F_{T0}		$F_T = F_{T0} + \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right) F_{A0}X$
			$F_T = F_{T0} + \delta F_{A0}X$

$$\Theta_B = \frac{F_{B0}}{F_{A0}} = \frac{C_{B0} v_0}{C_{A0} v_0} = \frac{C_{B0}}{C_{A0}} = \frac{y_{B0}}{y_{A0}}$$

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3.6 Flow Systems

- In general form, the molar flow rate of species i is:

$$F_i = F_{A0} (\Theta_i + \nu_i X)$$

- How to find F_T from the above equation?

$$F_T = \sum F_i = \sum F_{A0} (\Theta_i + \nu_i X) = F_{T0} + \delta F_{A0} X$$

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3.6.1 Equations for Concentrations in Flow Systems

- Convert F_A to C_A for a flow system.

$$C_A = \frac{F_A}{v} = \frac{\text{moles/time}}{\text{liters/time}} = \frac{\text{moles}}{\text{liter}} \quad \therefore C_i(X) = \frac{F_i(X)}{v(X)}$$

- The general equation can therefore be rewritten as:

$$C_i = \frac{F_{A0} (\Theta_i + \nu_i X)}{v(X)}$$

- Now we only need to find $v(X)$ to obtain $C_i(X)$.

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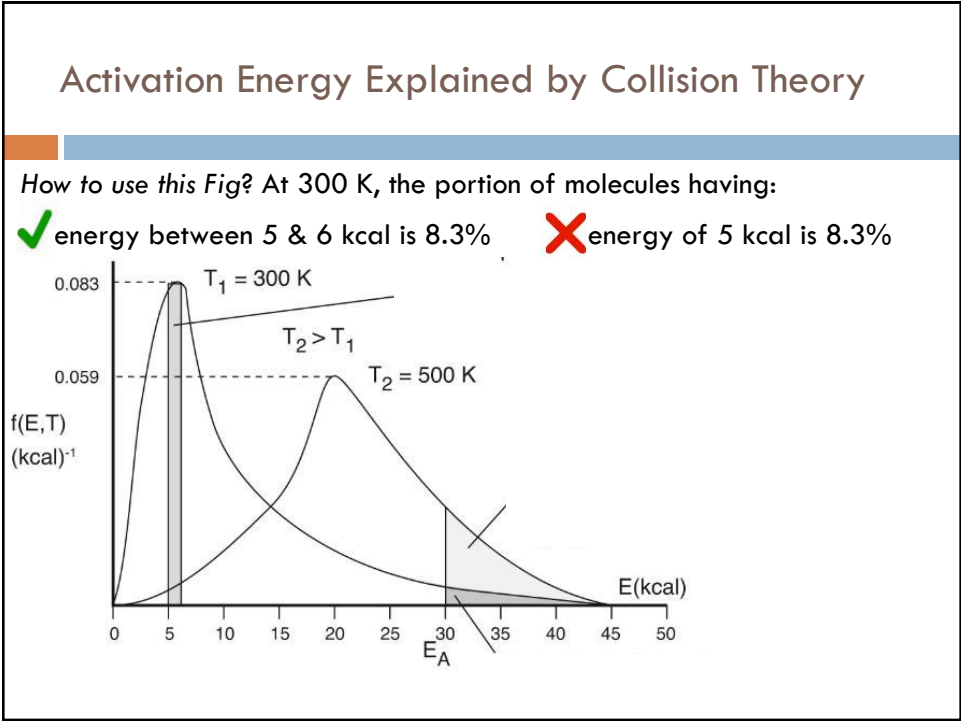
Lecture 14

Tutorial

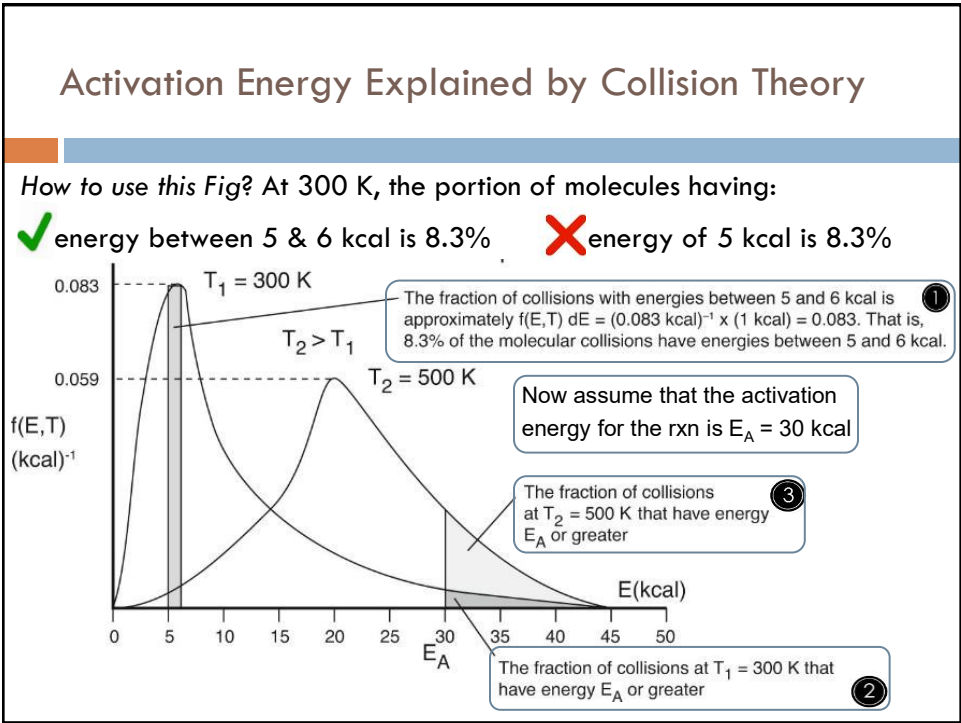
132

- In statistics, this Fig. is known as the Probability Density Function (f) & its integral over the entire space = 1.
- This Fig. is used to calculate the probability of E falling within a range, as opposed to taking on any one value.

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Comments on the $k(T)$

$k_A(T) = Ae^{-E/RT}$

- The rate of rxn increases with the increase of T .
- Use the following eq. to calculate the ratio $k_2(310K)/k_1(300K)$ for different rxns (i.e. for different E): $k_2 = k_1 e^{-\frac{E}{R}(\frac{1}{T_2} - \frac{1}{T_1})}$

rxn	E_a , kJ/mol	k_{310}/k_{300}
A + B → D	55	2.0
A + B → U	107	4.0
C → 2E	150	7.0
C + E → F	200	13.3

- The larger the E_a , the more temperature-sensitive is the rate of rxn.
- Why? (Refer to the $f(E,T)$ vs E Fig.)

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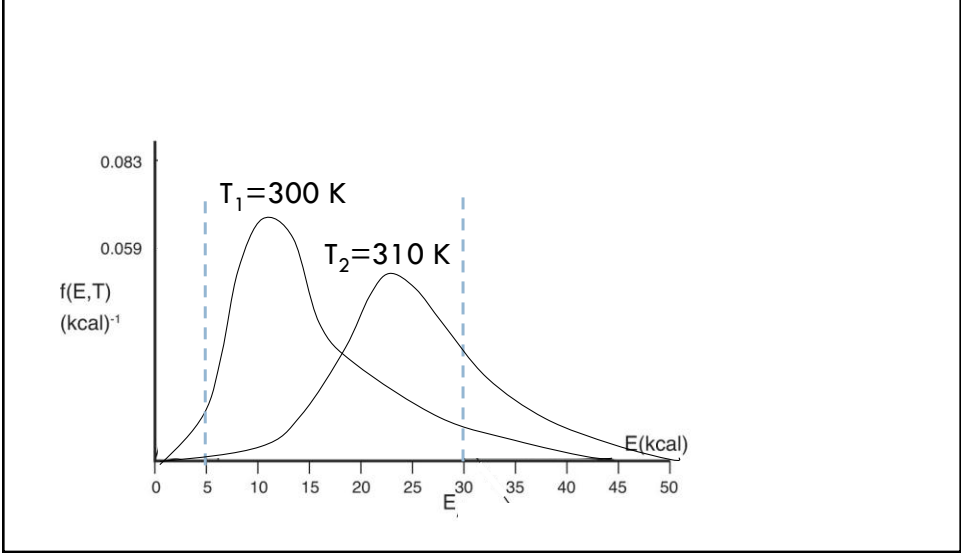
The sensitivity of k to temperature

- Which reaction rate or rate constant is more sensitive to temperature? Why?

(The k for the rxn with $E = 55$ kJ/mol or that with $E = 150$ kJ/mol?)

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The sensitivity of k to temperature, why?



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Test yourself at Home! (will be needed for problem 4-9)



20 min

A reversible liquid-phase isomerization $A \rightleftharpoons B$ is carried out *isothermally* in a 1000-gal CSTR. The reaction is second order in both the forward and reverse directions. The reaction is reversible with $K_C = 3.0$ at 300 K, and $\Delta H^\circ_{R_{rx}} = -25,000$ cal/mol.

$$K_C(T) = K_C(T_0) \exp \left[\frac{\Delta H^\circ_{R_{rx}}}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right]$$

1. Derive the rate law for this non-elementary rxn.

2. What is the expression of K_c used in the rate law?

$\ln K$

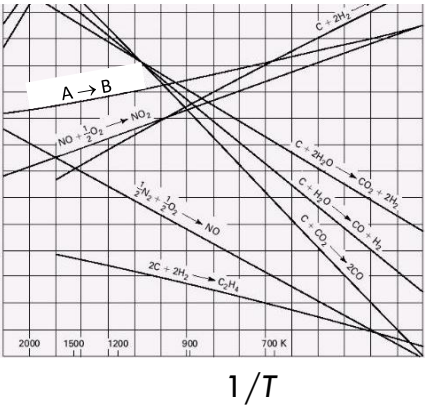
3. What is the expression of the given K_c ?

4. What is the relationship between K_c & $(K_c)_{\text{given}}$?

5. What are the values of T_0 , $K_c(T_0)$, & $\Delta H^\circ_{\text{rxn}}$ that will be used in the K_c equation above?

6. Calculate the rate law K_c at 310K.

[Answer: 0.60]



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P 3-2

35 min

(h) The rate law for the reaction $(2A + B \rightarrow C)$ is $-r_A = k_A C_A^2 C_B$ with $k_A = 25(\text{dm}^3/\text{mol})^2/\text{s}$. What are k_B and k_C ?

(i) At low temperatures the rate law for the reaction $(\frac{1}{2}A + \frac{3}{2}B \rightarrow C)$ is $-r_A = k_A C_A C_B$. If the reaction is reversible at high temperatures, what is the rate law?

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Reactive Reflections & Golden Notes

خواطر تفاعلية وفوائد ذهبية

Probability Distribution:

1. Discrete Probability Distribution

probability mass function

discrete random variable: takes on a finite or countably number of possible values

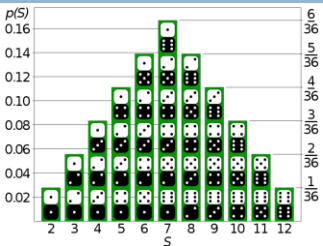
https://en.wikipedia.org/wiki/Probability_distribution

2. Continuous probability distribution

probability density function

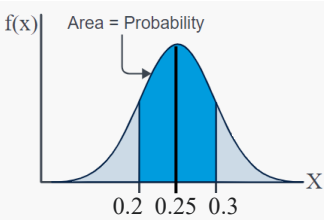
continuous random variable: takes on an uncountable infinite number of possible values

<https://online.stat.psu.edu/stat414/lesson/14/14.1>



Sum (S)	Probability p(S)
2	1/36
3	2/36
4	3/36
5	4/36
6	5/36
7	6/36
8	5/36
9	4/36
10	3/36
11	2/36
12	1/36

sum S of counts from two dice



Area = Probability

mass of quarter pounder burger

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Lecture 15

Writing $V(X)$ & $v(X)$

Prepared by: Dr Shaker Haji - CHENG 323

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Equations for Concentrations as function of Conversion

□ Batch System:

$$C_i(X) = \frac{N_i(X)}{V(X)}$$

$$N_i = N_{A0} (\Theta_i + \nu_i X)$$

□ Flow System:

$$C_i(X) = \frac{F_i(X)}{v(X)}$$

$$F_i = F_{A0} (\Theta_i + \nu_i X)$$

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3.6.2 Liquid-Phase Concentrations

- For liquids, especially when the rxn mixture is predominantly solvent, volume change with rxn is negligible when no phase changes are taking place.

- Consequently, we can assume:

$$V = V_0 \text{ (Batch Reactors) or } \nu = \nu_0 \text{ (Flow Reactors)}$$

- Therefore, $C_i = f(X)$ can be rewritten as:

$$C_i = \frac{N_i}{V} = \frac{N_{A0}(\Theta_i + \nu_i X)}{V_0} \qquad C_i = \frac{F_i}{\nu} = \frac{F_{A0}(\Theta_i + \nu_i X)}{\nu_0}$$

$$C_i = C_{A0}(\Theta_i + \nu_i X) \qquad C_i = C_{A0}(\Theta_i + \nu_i X)$$

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3.6.3 Gas-Phase Concentrations

For Liquid-Phase RXNS:

$$V = V_0 \text{ (Batch Reactors) or } \nu = \nu_0 \text{ (Flow Reactors)} \mapsto C_i = C_{A0}(\Theta_i + \nu_i X)$$

For Gas-Phase RXNS:

- Gas volume or volumetric flow rate is a strong function of:
 - ▢ the total number of moles
 - ▢ Temperature
 - ▢ Pressure
- Therefore, one cannot always use the above eqn. to express $C_i(X)$ for gas-phase rxns.
- Now we will consider cases where V or ν vary as the rxn progresses.

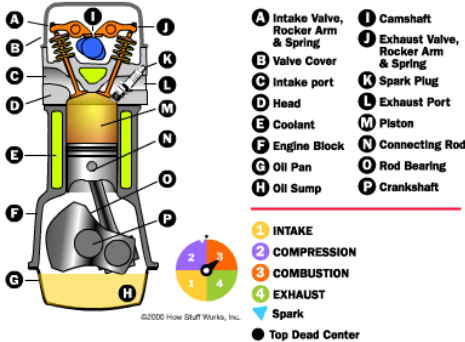
145

1) Variable-Volume Reactors

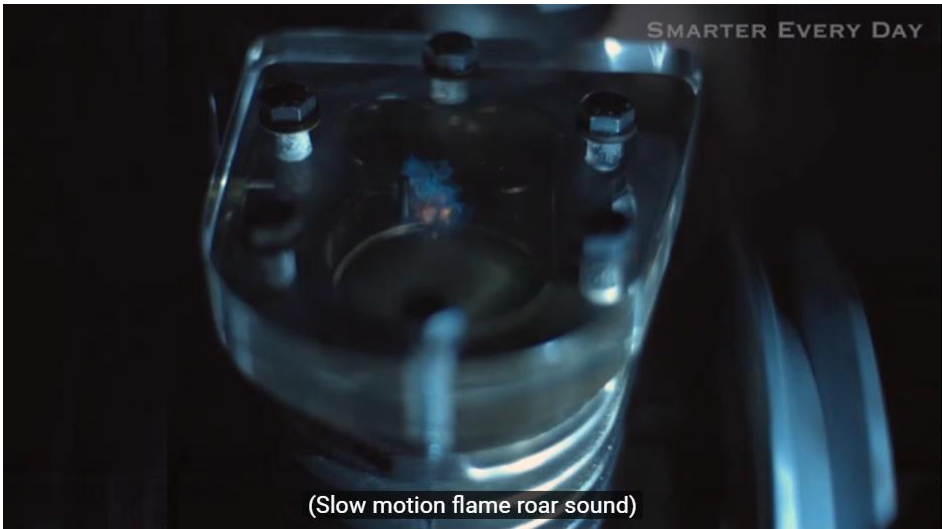
- Although variable volume batch reactors are seldom encountered in labs or industry, they have been used to collect rxn data for gas-phase rxns.
- An everyday example of a variable-volume batch reactor is:

- the combustion chamber of the internal-combustion engine (during the combustion stroke)

Source: www.howstuffworks.com



146

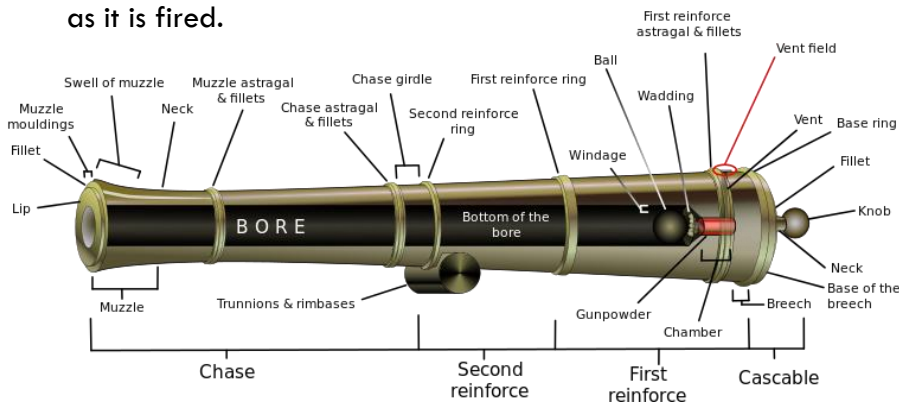


Youtube: How Engines Work - (See Through Engine in Slow Motion) - Smarter Every Day 166

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Variable-Volume Reactors

- Another example of a variable-volume batch reactor is:
 - ▣ the expanding gases within the breech and barrel of a firearm as it is fired.



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3.6.3 Gas-Phase Concentrations Variable-Volume Reactors

$$N_i = N_{A0} (\Theta_i + \nu_i X)$$

- Q: The N_i expression, that we recently derived, can it be used in both constant-volume and varying-volume cases?
- ANS: Yes.
- It's the $C_i(X)$ that are not the same in these two cases.
- To write $C_i(X)$ for gas-phase rxns, first find $V = f(X)$! How?
- By using the an appropriate equation of state; e.g.:

$$PV = ZN_T RT$$

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Variable-Volume Reactors

$$PV = ZN_T RT$$

in which V = volume
 N_T = total number of moles
 T = temperature, K
 P = total pressure, atm (kPa; 1 atm = 101.3 kPa)
 Z = compressibility factor
 R = gas constant = 0.08206 dm³ · atm/mol · K

□ This equation is valid at any point in the system at any time t .

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Batch Reactors with Variable Volume:

Finding $V = f(X)$



10 min

$PV = ZN_T RT$ and at time $t=0$, $P_0 V_0 = Z_0 N_{T0} RT_0$

□ Upon manipulations:
$$V = V_0 \left(\frac{P_0}{P} \right) \frac{T}{T_0} \left(\frac{Z}{Z_0} \right) \frac{N_T}{N_{T0}}$$

□ However, we want $V = f(X)$!

□ Find N_T/N_{T0} as a function of X using:

$$N_T = N_{T0} + \delta N_{A0} X$$

Stoichiometric Table for a Batch Systems $A + \frac{b}{a} B \longrightarrow \frac{c}{a} C + \frac{d}{a} D$

Species	Initially (mol)	Change (mol)	Remaining (mol)
A	N_{A0}	$N_A - N_{A0} = -N_{A0} X$	$N_A = N_{A0} - N_{A0} X$
B	N_{B0}	$-b/a N_{A0} X$	$N_B = N_{B0} - b/a N_{A0} X$
C	N_{C0}	$+c/a N_{A0} X$	$N_C = N_{C0} + c/a N_{A0} X$
D	N_{D0}	$+d/a N_{A0} X$	$N_D = N_{D0} + d/a N_{A0} X$
I (inert)	N_{I0}	no change	$N_I = N_{I0}$
Totals	N_{T0}		$N_T = N_{T0} + \delta N_{A0} X$

$\delta = (d/a + c/a - b/a - 1)$

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Batch Reactors with Variable Volume:**Finding $V = f(X)$**

$$C_i = \frac{N_{A0}(\Theta_i + v_i X)}{V}$$

$$PV = ZN_T RT \quad \text{and at time } t=0, \quad P_0 V_0 = Z_0 N_{T0} R T_0$$

□ Upon manipulations:
$$V = V_0 \left(\frac{P_0}{P} \right) \frac{T}{T_0} \left(\frac{Z}{Z_0} \right) \frac{N_T}{N_{T0}}$$

□ However, we want $V = f(X)$!

□ Find N_T/N_{T0} as a function of X using: $N_T = N_{T0} + \delta N_{A0} X$

□ $N_T/N_{T0} = 1 + y_{A0} \delta X$

□ Define $\varepsilon = y_{A0} \delta$ as the **molar expansion factor**

□ Now we have:
$$\frac{N_T}{N_{T0}} = 1 + \varepsilon X$$

□ Substitute in the above V equation...

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Batch Reactors with Variable Volume

$$V = V_0 \left(\frac{P_0}{P} \right) \frac{T}{T_0} \left(\frac{Z}{Z_0} \right) \frac{N_T}{N_{T0}}$$

□ Upon substitution:
$$V = V_0 \left(\frac{Z}{Z_0} \right) (1 + \varepsilon X) \left(\frac{T}{T_0} \right) \left(\frac{P_0}{P} \right)$$

□ In the gas-phase systems that we shall be studying, the T & P are such that the Z will not change significantly during the course of the reaction: hence $Z=Z_0$, therefore,

$$V = V_0 (1 + \varepsilon X) \left(\frac{T}{T_0} \right) \left(\frac{P_0}{P} \right)$$

□ This eqn. must be used for a **variable-volume batch reactor** to find $V(X)$.

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Notes

- Is the above eq. correct in a constant-volume situation?
- Is it useful even in a constant-volume situation?
- Yes, it gives $P = f(T, X)$

$$V = V_0(1 + \varepsilon X) \left(\frac{T}{T_0} \right) \left(\frac{P_0}{P} \right)$$

Determine the Pressure at the calculated time

How Long Does the RXN Take?

CDPI-A:
A 200-L constant-volume batch reactor is pressurized to 20 atm with a mixture of 75% A and 25% inert. The gas-phase reaction ($A \rightarrow B + C$) is carried out isothermally at 227°C.

- Assuming that the ideal gas law is valid, how many moles of A are in the reactor initially? What is the initial concentration of A?
($R = 0.08206 \text{ L atm/mol K}$)
- If the reaction is first order, $-r_A = kC_A$ with $k = 0.1 \text{ min}^{-1}$, calculate the time necessary to consume 99% of A.
- Determine the pressure at the calculated time

$N_{A0} = 73.1 \text{ mol}, C_{A0} = 0.365 \text{ M}, t = 46 \text{ min}, P = 34.85 \text{ atm}$



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Notes

- What does ε ($\varepsilon = y_{A0} \delta$, the molar expansion factor) represents?

$$\frac{N_T}{N_{T0}} = 1 + \varepsilon X$$
→

$$\varepsilon = \frac{N_T - N_{T0}}{N_{T0} X}$$

or at complete conversion:

$$\varepsilon = \frac{N_{Tf} - N_{T0}}{N_{T0}} = \frac{\text{Change in total number of moles for complete conversion}}{\text{Total moles fed}}$$



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2) Continuous Flow Reactors with Variable Volumetric Flow Rate



- A situation where one encounters a varying flow rate occurs quite frequently in gas-phase rxns that do not have an equal number of product and reactant moles.
- For example, $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$
- What happens to the F_T & v as the above rxn progresses?
- In flow systems where this type of rxn occurs, the molar flow rate and hence the volume flow rate will be changing as the rxn progresses.

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Flow Reactors with Variable Volumetric Flow Rate: Finding $C_i = f(X)$ or $C_i = f(F)$

$$C_i = \frac{F_{A0}(\Theta_i + \nu_i X)}{v(X)}$$

Requirement 1: $C_i = f(X)$ through $v = f(X)$

- For a batch system: $V = V_0(1 + \varepsilon X) \left(\frac{T}{T_0} \right) \left(\frac{P_0}{P} \right)$
- Similarly, for a flow system: $v = v_0(1 + \varepsilon X) \left(\frac{T}{T_0} \right) \left(\frac{P_0}{P} \right)$
- Since $C_i = F_i/v$, therefore,

$$C_i = C_{A0} \frac{(\Theta_i + \nu_i X)}{(1 + \varepsilon X)} \frac{T_0}{T} \frac{P}{P_0}$$

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Flow Reactors with Variable Volumetric

Flow Rate: Finding $C_i = f(X)$ or $C_i = f(F)$

Requirement 2: $C_i = f(F)$

- Knowing that $C_i = F_i/v$, how can we write $C_i = f(F)$?
- Find v as $f(F)$ rather than $f(X)$. How?
- For a gas-phase rxn, $v = Z \frac{F_T RT}{P}$ and $v_0 = Z_0 \frac{F_{T0} RT_0}{P_0}$
- Upon rearrangement & neglecting the change in Z :

$$v = v_0 \left(\frac{F_T}{F_{T0}} \right) \left(\frac{T}{T_0} \right) \left(\frac{P_0}{P} \right)$$
- Since $C_i = F_i/v$, therefore, $C_i = C_{T0} \left(\frac{F_i}{F_T} \right) \left(\frac{T_0}{T} \right) \left(\frac{P}{P_0} \right)$
- This form of C_i is used for membrane reactors & multiple rxns.

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Timeout: is there an equation for $V_{\text{liquid}}(T, P)$?

$$\beta \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad \text{Volume expansivity} \quad \kappa \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad \text{Isothermal compressibility}$$

CHENG 211:
Chapter 3 in
Introduction to
Chemical Eng
Thermodynamics
by Smith, Van
Ness, & Abbott

$$\frac{dV}{V} = \beta dT - \kappa dP$$

$$\ln \frac{V_2}{V_1} = \beta (T_2 - T_1) - \kappa (P_2 - P_1)$$

Example 3.1:

For liquid acetone at 20°C and 1 bar,

$$\beta = 1.487 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}, \quad \kappa = 62 \times 10^{-6} \text{ bar}^{-1}, \quad V = 1.287 \text{ cm}^3 \text{ g}^{-1}$$

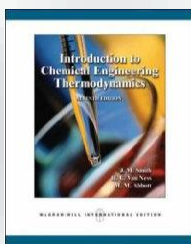
For acetone, find:

a) The value of $\left(\frac{\partial P}{\partial T} \right)_V$ at 20°C and 1 bar.

b) The pressure generated by heating at constant V from 20°C and 1 bar to 30°C.

c) The change in volume for a change from 20°C and 1 bar to 0°C and 10 bar.

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Determining $C_i = f_i(X)$ for a Gas-Phase Reaction

40 min

Alternative Example (3-6)

The reversible gas-phase oxidation rxn of nitric oxide (NO) to nitrogen dioxide (NO₂),
$$\text{NO} + \frac{1}{2} \text{O}_2 \leftrightarrow \text{NO}_2$$
is to be carried out at constant temperature of 770 K. The feed consists of NO with a partial pressure of 0.259 atm and 20% excess air.

1. Determine the value of the concentration equilibrium constant, K_c , for the given rxn at 770 K.

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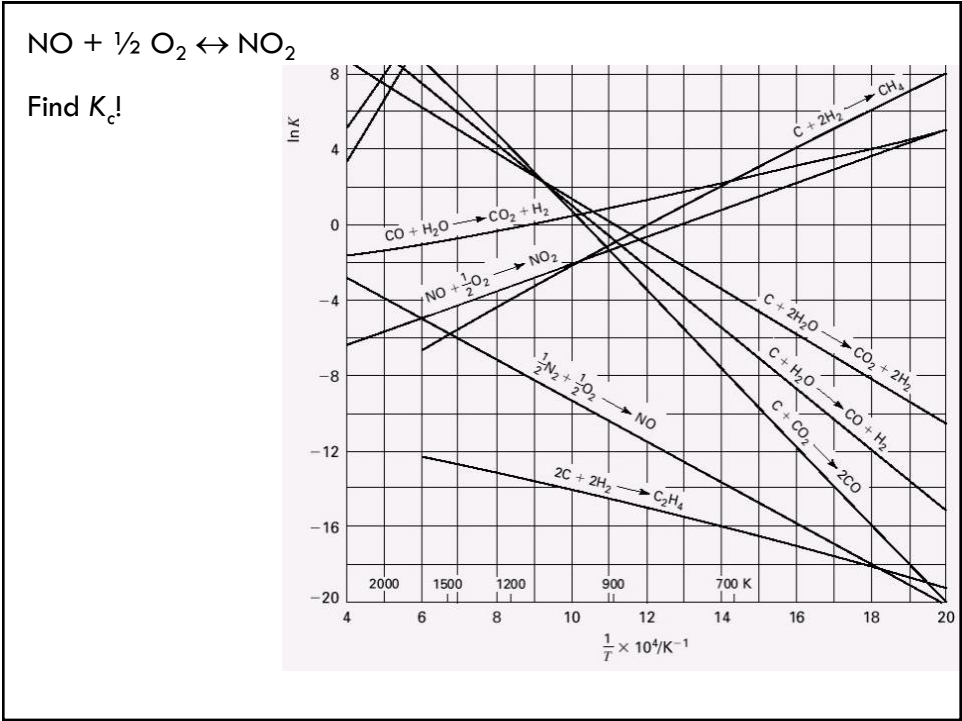
1. Determine the value of the conc. equilibrium const., K_c , for the given rxn at 770 K.

Fig. Equilibrium constants as a function of temperature for selected reactions.

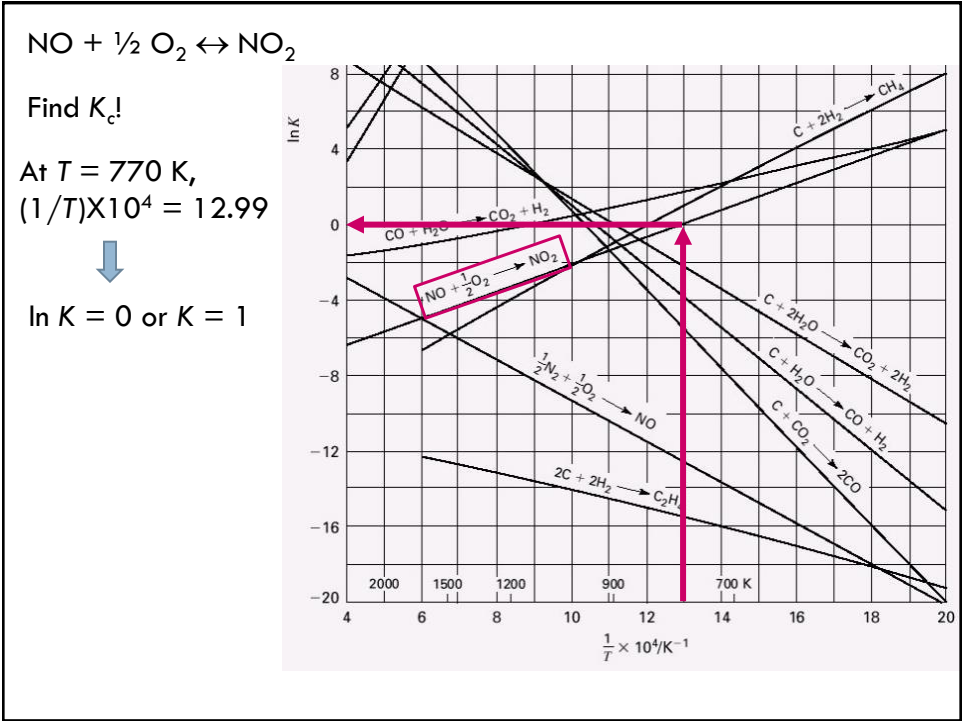
*"Introduction to Chemical Engineering Thermodynamics",
Smith J.M., Van Ness H.C. & Abbott M.M., 7th Ed., McGraw-Hill,
New York, 2005.*

The graph plots the natural logarithm of the equilibrium constant, $\ln K$, on the y-axis (ranging from -20 to 28) against the reciprocal of temperature, $1/T \times 10^4 / \text{K}^{-1}$, on the bottom x-axis (ranging from 4 to 20). A secondary top x-axis shows temperature in Kelvin (2000, 1500, 1200, 900, 700 K). Several linear data series are shown, each corresponding to a specific chemical reaction. The reactions include: $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$, $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{H}_2\text{O}$, $\text{CO} + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{CO}_2$, $\text{C} + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{CO}$, $\text{C} + \text{O}_2 \rightleftharpoons \text{CO}_2$, $\text{C} + 2\text{H}_2 \rightleftharpoons \text{CH}_4$, $\text{C} + 2\text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 2\text{H}_2$, $\text{C} + \text{H}_2\text{O} \rightleftharpoons \text{CO} + \text{H}_2$, $\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO}$, $\frac{1}{2} \text{N}_2 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{NO}$, $2\text{C} + 2\text{H}_2 \rightleftharpoons \text{C}_2\text{H}_4$, and $\text{NO} + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{NO}_2$ (the reaction of interest).

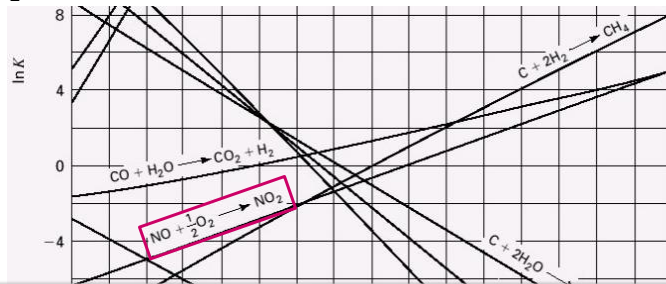
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$$K = K_c \cdot (RT / P^0)^\delta$$

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Lecture 16

Tutorial

Prepared by: Dr Shaker Haji - CHENG 323

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Determining $C_i = h_i(X)$ for a Gas-Phase Reaction

Alternative to Example (3-6)

The reversible gas-phase oxidation rxn of nitric oxide (NO) to nitrogen dioxide (NO_2),

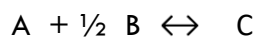
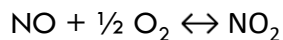
$$\text{NO} + \frac{1}{2} \text{O}_2 \leftrightarrow \text{NO}_2$$

is to be carried out at constant temperature of 770 K. The feed consists of NO with a partial pressure of 0.259 atm and 20% excess air.

1. Determine the value of the conc. equilibrium const., K_c , for the given rxn at 770 K.
2. Calculate the equilibrium conversion, X_e , of NO in a constant-volume batch reactor.
3. Calculate the X_e in a flow reactor.
4. Assuming the rxn follows an elementary rate law, express the rate of rxn solely as a function of X for a flow system and for a constant- V batch system.
5. Determine the CSTR volume necessary to achieve 80% of the X_e .

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The reversible gas-phase combustion of nitric oxide (NO)



is to be carried out at constant temperature of 770 K. The feed consists of NO with a partial pressure of 0.259 atm and 20% excess air.

2. Calculate X_e of NO in a constant-volume batch reactor.

$$K_c = \frac{C_{\text{NO}_2e}}{C_{\text{NO}e} \cdot C_{\text{O}_2e}^{0.5}}$$

$$K_c = \frac{C_{\text{Ce}}}{C_{\text{Ae}} \cdot C_{\text{Be}}^{0.5}}$$

$$C_i = N_i / V$$

$$C_i = N_{\text{A}0} (\Theta_i + \nu_i X) / V_0$$

$$C_i = C_{\text{A}0} (\Theta_i + \nu_i X)$$

$$C_{\text{Ae}} = C_{\text{A}0} (1 - X_e)$$

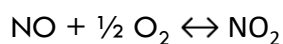
$$C_{\text{Be}} = C_{\text{A}0} (\Theta_{\text{B}} - 0.5 X_e)$$

$$C_{\text{Ce}} = C_{\text{A}0} (\Theta_{\text{C}} + X_e)$$

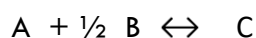
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The reversible gas-phase combustion of nitric oxide (NO)

$$P_{\text{A}0} = 0.259 \text{ atm}$$



$$C_{\text{A}0} = P_{\text{A}0} / RT$$



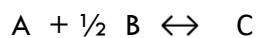
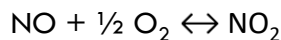
$$C_{\text{Ae}} = C_{\text{A}0} (1 - X_e)$$

$$C_{\text{Be}} = C_{\text{A}0} (\Theta_{\text{B}} - 0.5 X_e)$$

$$C_{\text{Ce}} = C_{\text{A}0} (\Theta_{\text{C}} + X_e)$$

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The reversible gas-phase combustion of nitric oxide (NO)



is to be carried out at constant temperature of 770 K. The feed consists of NO with a partial pressure of 0.259 atm and 20% excess air.

2. Calculate X_e of NO in a constant-volume batch reactor.

$K_c = \frac{C_{\text{NO}_2e}}{C_{\text{NO}e} \cdot C_{\text{O}_2e}^{0.5}}$	$C_i = N_i / V$	$P_{\text{A}0} = 0.259 \text{ atm}$
	$C_i = N_{\text{A}0} (\Theta_i + \nu_i X) / V_0$	$P_{\text{B}0} = 0.156 \text{ atm}$
	$C_i = C_{\text{A}0} (\Theta_i + \nu_i X)$	$P_{\text{I}0} = P_{\text{N}_2,0} = 0.585 \text{ atm}$
$K_c = \frac{C_{\text{C}e}}{C_{\text{A}e} \cdot C_{\text{B}e}^{0.5}}$	$C_{\text{A}e} = C_{\text{A}0} (1 - X_e)$	$P_0 = 1 \text{ atm}$
	$C_{\text{B}e} = C_{\text{A}0} (\Theta_{\text{B}} - 0.5 X_e)$	$\Theta_{\text{B}} = 0.6,$
	$C_{\text{C}e} = C_{\text{A}0} (\Theta_{\text{C}} + X_e)$	$\Theta_{\text{C}} = 0, \Theta_{\text{I}} = 2.26$
		$C_{\text{A}0} = P_{\text{A}0} / RT$
		$= 0.0041 \text{ mol/L}$

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$K_c = 8 \text{ (mol/L)}^{-0.5}$	$C_{\text{A}e} = C_{\text{A}0} (1 - X_e)$	$P_{\text{A}0} = 0.259 \text{ atm}$
$K_c = \frac{C_{\text{C}e}}{C_{\text{A}e} \cdot C_{\text{B}e}^{0.5}}$	$C_{\text{B}e} = C_{\text{A}0} (0.6 - 0.5 X_e)$	$P_{\text{B}0} = 0.156 \text{ atm}$
	$C_{\text{C}e} = C_{\text{A}0} X_e$	$P_{\text{I}0} = 0.585 \text{ atm}$
		$P_0 = 1 \text{ atm}$
		$\Theta_{\text{B}} = 0.6,$
		$\Theta_{\text{C}} = 0, \Theta_{\text{I}} = 2.26$
		$C_{\text{A}0} = P_{\text{A}0} / RT$
		$= 0.0041 \text{ mol/L}$

$$8 = \frac{C_{\text{A}0} X_e}{C_{\text{A}0} (1 - X_e) \cdot [C_{\text{A}0} (0.6 - 0.5 X_e)]^{0.5}}$$

$$8 = \frac{X_e}{(1 - X_e) \cdot (0.0041)^{0.5} (0.6 - 0.5 X_e)^{0.5}}$$

$$X_e = 0.260$$

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3. Calculate the X_e in a flow reactor.

$K_C = 8 \text{ (mol/L)}^{-0.5}$ $C_i = F_i / v$

$K_C = \frac{C_{Ce}}{C_{Ae} \cdot C_{Be}^{0.5}}$



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3. Calculate the X_e in a flow reactor.

$K_C = 8 \text{ (mol/L)}^{-0.5}$ $C_i = F_i / v$

$K_C = \frac{C_{Ce}}{C_{Ae} \cdot C_{Be}^{0.5}}$ $v = v_0 (1 + \epsilon X) \left(\frac{T}{T_0} \right) \left(\frac{P_0}{P} \right)$ $C_i = \frac{F_{A0} (\Theta_i + \nu_i X)}{v_0 (1 + \epsilon X)}$ $C_i = \frac{C_{A0} (\Theta_i + \nu_i X)}{(1 + \epsilon X)}$

NO + 1/2 O₂ ↔ NO₂
A + 1/2 B ↔ C

$P_{A0} = 0.259 \text{ atm}$ $P_{B0} = 0.156 \text{ atm}$ $P_{I0} = 0.585 \text{ atm}$ $P_{T0} = P_T = 1 \text{ atm}$

(assuming $\Delta P = 0$)

 $\Theta_B = 0.6,$ $\Theta_C = 0, \Theta_I = 2.26$ $C_{A0} = P_{A0} / RT$ $= 0.0041 \text{ mol/L}$ $y_{A0} = 0.259$ $\epsilon = (0.259)(-0.5)$ $= -0.1295$

* Isothermal operation & assuming negligible pressure drop

$8 = \frac{X_e (1 + \epsilon X_e)^{0.5}}{(1 - X_e) \cdot (C_{A0})^{0.5} (0.6 - 0.5 X_e)^{0.5}}$ $X_e = 0.263$

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$$\text{NO} + \frac{1}{2} \text{O}_2 \leftrightarrow \text{NO}_2$$

Constant-volume batch system: $X_e = 0.260$

Flow System: $X_e = 0.263$





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4. Assuming the rxn follows an elementary rate law, express the rate of rxn solely as a function of X for a constant- V batch system and a flow system.

$$\text{NO} + \frac{1}{2} \text{O}_2 \leftrightarrow \text{NO}_2$$

$$-r_A = k_A \left(C_A \cdot C_B^{0.5} - \frac{C_C}{K_c} \right)$$

$$C_i = C_{A0} (\Theta_i + \nu_i X)$$

$$C_i = \frac{C_{A0} (\Theta_i + \nu_i X)}{(1 + \varepsilon X)}$$

Constant-volume batch system:

$$-r_A = k_A \left((0.0041)^{1.5} (1 - X) (0.6 - 0.5X)^{0.5} - \frac{(0.0041)X}{7.949} \right)$$

Flow System:

$$-r_A = k_A \left(\frac{(0.0041)^{1.5} (1 - X) (0.6 - 0.5X)^{0.5}}{(1 - 0.1295X)^{1.5}} - \frac{(0.0041)X}{7.949 \cdot (1 - 0.1295X)} \right)$$

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5. Determine the CSTR volume necessary to achieve 80% of the X_e .

Assume $k_A = 10 \text{ (L}^{0.5}/\text{mol}^{0.5}/\text{min)}$ & $F_{A0} = 1 \text{ mol/min}$

Should we use the variable-density or constant-density concentration expressions for CSTR in this example?

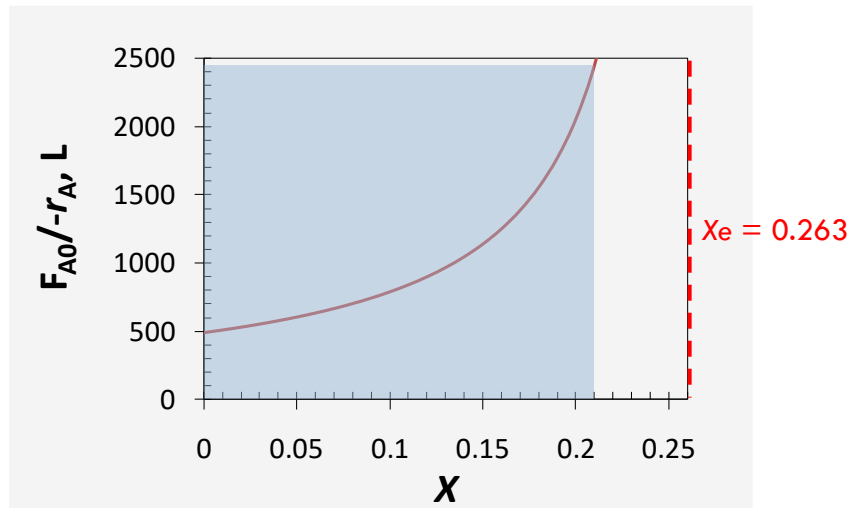
Of course variable-density (variable-volumetric flow rate) concentration expressions, because $v \neq v_0$

For flow system, $X_e = 0.263$, so 80% of X_e represents $X = 0.21$

$$-r_A = 10 \left(\frac{(0.0041)^{1.5} (1-X)(0.6-0.5X)^{0.5}}{(1-0.1295X)^{1.5}} - \frac{(0.0041)X}{7.949 \cdot (1-0.1295X)} \right)$$

$$V = \frac{F_{A0}}{-r_A|_{exit}} X$$

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$$V = \frac{F_{A0}}{-r_A|_{exit}} X = 2455 \cdot 0.21 = 516 \text{ L}$$

Review the "Test yourself" questions at the end of Chap 3 slides.

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Closure

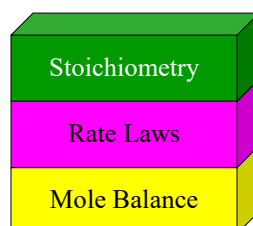
Mole Balance

Rate Laws

Stoichiometry

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Closure



- We have now completed the first three basic building blocks in our algorithm to study isothermal chemical reactions and reactors.
- In Chap. 4, we will focus on the **combine** and **evaluation** building blocks which will then complete our algorithm for isothermal chemical reactor design.

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Note 1

Note 2

Complete Suggested Problems

#4

Quiz

#3

one week from
today

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Test Yourself, Alternative to Example (3-6)

The reversible gas-phase oxidation rxn of nitric oxide (NO) to nitrogen dioxide (NO₂), $2 \text{ NO} + \text{O}_2 \leftrightarrow 2 \text{ NO}_2$

is to be carried out at constant temperature of 770 K. The feed consists of NO with a partial pressure of 0.259 atm and 20% excess air.

1. Determine the value of the conc. equilibrium const., K_c , for the given rxn at 770 K.

Answer: $K_c = 64 \text{ L/mol}$

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Test Yourself, Alternative to Example (3-6)

The reversible gas-phase oxidation rxn of nitric oxide (NO) to nitrogen dioxide (NO₂), $2 \text{ NO} + \text{O}_2 \leftrightarrow 2 \text{ NO}_2$

is to be carried out at constant temperature of 770 K. The feed consists of NO with a partial pressure of 0.259 atm and 20% excess air.

2. Calculate the equilibrium conversion, X_e , of NO in a flow reactor.

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Test Yourself, Alternative to Example (3-6)

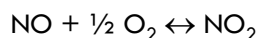
2. Calculate the equilibrium conversion, X_e , of NO in a flow reactor.

Hint: You may use any of the following expressions for K_c :

$$K_c = \frac{C_{\text{NO}_2e}}{C_{\text{NO}e} \cdot C_{\text{O}_2e}^{0.5}} = 8, \text{ or } K_c = \frac{C_{\text{NO}_2e}^2}{C_{\text{NO}e}^2 \cdot C_{\text{O}_2e}} = 64,$$

$$\text{or even } K_c = \frac{C_{\text{NO}_2e}^3}{C_{\text{NO}e}^3 \cdot C_{\text{O}_2e}^{1.5}} = 512$$

However, X , v_i , δ , and ε should all be based on the stoichiometric equation where NO, the limiting reactant, is the basis of the calculation:



Answer: $X_e = 0.263$

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Test Yourself, Alternative to Example (3-6)

The reversible gas-phase oxidation rxn of nitric oxide (NO) to nitrogen dioxide (NO₂), $2 \text{ NO} + \text{O}_2 \leftrightarrow 2 \text{ NO}_2$

is to be carried out at constant temperature of 770 K. The feed consists of NO with a partial pressure of 0.259 atm and 20% excess air.

3. Calculate the equilibrium conversion, X_e , of NO in a flow reactor if the excess air was increased to 60%.

Answer: $X_e = 0.296$

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Test Yourself, Alternative to Example (3-6)

The reversible gas-phase oxidation rxn of nitric oxide (NO) to nitrogen dioxide (NO₂), $2 \text{ NO} + \text{O}_2 \leftrightarrow 2 \text{ NO}_2$

is to be carried out at constant temperature of 770 K. The feed consists of NO with a partial pressure of 0.259 atm and 20% excess air.

4. Derive the rate law, assuming the rxn follows an elementary rate law.

Answer: $-r_A = k_A \left(C_{\text{NO}}^2 \cdot C_{\text{O}_2} - \frac{C_{\text{NO}_2}^2}{K_c} \right)$, where $K_c = \frac{C_{\text{NO}_2e}^2}{C_{\text{NOe}}^2 \cdot C_{\text{O}_2e}}$

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Test Yourself & Reflect at Home:

Reflect on this rate law; what can you learn?

Reaction Rate ^[3,4,5,6,7,8]

To calculate the rate of reaction, modified Temkin equation offered by Dyson & Simon in 1968 has been used ^[4]

$$R_{NH_3} = 2k \left[K_a^2 a_{N_2} \left(\frac{a_{H_2}^3}{a_{NH_3}^2} \right)^\alpha - \left(\frac{a_{NH_3}^2}{a_{H_2}^3} \right)^{1-\alpha} \right]$$

in which

α : Constant which takes a value from 0.5 to 0.75 in literature ^[8].

k : Rate constant for reverse reaction in: $N_2 + 3H_2 \rightleftharpoons 2NH_3$

K_a : equilibrium constant

a_i : Activity

Available online at www.vurup.sk/pc
Petroleum & Coal 48 (2), 15-23, 2006

MODELING AND SIMULATION OF AMMONIA SYNTHESIS REACTOR

Ali Dashti, Kayvan Khorsand¹, Mehdi Ahmadi Marvast, Madjid Kakavand