

A. Svistunov, A. Fetisova, T. Litvinova

# **TEXTBOOK**

Fundamentals of Terminology, Reading,
Interpreting and Solving Problems in Chemistry
in English
General Chemistry

Advanced Level

Федеральное государственное бюджетное образовательное учреждение высшего образования Первый Московский государственный медицинский университет имени И.М. Сеченова Министерства здравоохранения Российской Федерации

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**A.** Svistunov, A. Fetisova, T. Litvinova. Fundamentals of terminology, reading, interpreting and solving problems in chemistry in English. General Chemistry. Advanced Level. Textbook.-M: I.M. Sechenov First MSMU, 2016.

Учебное пособие является основой образовательного курса довузовской подготовки для профильных классов медицинской направленности «Химия на английском» для учащихся средних образовательных школ. Методологическая система курса ориентирована на эффективное усвоение знаний и отработку умений учащихся при чтении, интерпретации и решении заданий по химии на английском языке. Курс включает углубленное изучение избранных разделов общей химии на английском языке. Учебное пособие (Textbook) составляет единый учебно-методический комплекс с рабочей тетрадью (Workbook) и тестовой книжкой (Test Book).

Для учащихся 10-11-х профильных классов средних образовательных школ, изучающих химию по программам углубленной подготовки; преподавателей химии и английского языка; самостоятельного изучения основных разделов общей химии на английском языке и подготовке к сдаче экзаменов по химии в соответствии с международными программами.

Учебное пособие создано по приоритетному направлению **Развитие системы профильного** обучения в условиях интеграции общего и дополнительного образования.

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# Федеральное государственное бюджетное образовательное учреждение высшего образования Первый Московский государственный медицинский университет имени И.М. Сеченова Министерства здравоохранения Российской Федерации

#### РАБОЧАЯ ПРОГРАММА

Образовательного учебного курса для профильных классов медицинской направленности «ХИМИЯ НА АНГЛИЙСКОМ» для учащихся средних образовательных школ

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# 1. ЦЕЛИ И ЗАДАЧИ ОБРАЗОВАТЕЛЬНОГО УЧЕБНОГО КУРСА «ХИМИЯ НА АНГЛИЙСКОМ» ДЛЯ ПРОФИЛЬНЫХ КЛАССОВ МЕДИЦИНСКОЙ НАПРАВЛЕННОСТИ

#### ПОЯСНИТЕЛЬНАЯ ЗАПИСКА

Рабочая программа образовательного учебного курса для профильных классов медицинской направленности «Химия на английском» для учащихся средних образовательных школ составлена в соответствии с Федеральным законом ( $\Phi$ 3) от 29.12.2012 N 273- $\Phi$ 3 (ред. от 03.07.2016) "Об образовании в Российской Федерации" (с изм. и доп., вступ. в силу с 01.09.2016). Рабочая программа учитывает положения Статьи 14. Язык образования, в частности пункта 5, указывающего, что «образование может быть получено на иностранном языке в соответствии с образовательной программой и в порядке, vстановленном законодательством об образовании осуществляющей нормативными актами организации, образовательную деятельность», и *пункта* 6, указывающего, что «язык, языки образования локальными определяются нормативными актами организации, осуществляющей образовательную деятельность реализуемым ПО образовательным программам, в соответствии с законодательством Российской Федерации».

Содержание рабочей программы является интегрированным в методологическом плане и охватывает отдельные разделы смежных (и несмежных) учебных дисциплин.

Образовательный учебный курс для профильных классов медицинской направленности «Химия на английском» для учащихся средних образовательных школ (далее курс) ориентирован на довузовскую подготовку. В соответствии с основными задачами интеграции медицинского образования РФ в международное пространство высшего профессионального образования интенция курса предусматривает его внедрение в системе среднего (полного) общего образования и направлена на предметную профильную ориентацию учащихся школ-партнеров в образовательном пространстве ФГБОУ ВО Первый МГМУ им. И.М. Сеченова Минздрава России.

При построении рабочей программы курса предполагалось, что контингент обучаемых — это предметно-мотивированные учащиеся 10-11 профильных классов медицинской направленности, владеющие английским языком предпочтительно на уровне B1, B2, но не ниже уровня A2.

Методологическая система курса ориентирована на эффективное усвоение знаний и отработку умений учащихся при чтении, интерпретации и решении заданий по химии на английском языке.

Курс включает углубленное изучение избранных разделов общей химии на английском языке и предусматривает:

- > предметный терминологический тренинг на английском языке;
- чтение, интерпретацию и решение заданий по химии на английском языке;

- отработку практических навыков по интерпретации и решению заданий по химии на английском языке;
- систему контрольных тест-блоков для полного и выборочного тренинга по научной химической терминологии, контроля эффективности усвоения знаний учащимися и оценки уровня овладения практическими навыками при чтении, интерпретации и решении заданий по химии на английском языке;
- разбор тематических разделов программы и решение заданий международных экзаменов по химии.

# 2. ТРЕБОВАНИЯ К УРОВНЮ ОСВОЕНИЯ СОДЕРЖАНИЯ ОБРАЗОВАТЕЛЬНОГО УЧЕБНОГО КУРСА «ХИМИЯ НА АНГЛИЙСКОМ»

#### Обеспечиваемые компетенции

- 1. Владение культурой билингвального научного мышления, способность к восприятию информации, постановке цели и выбору путей ее достижения, анализу и обобщению.
- 2. Умение логически верно, аргументированно и ясно строить устную и письменную научную речь на английском языке.
- 3. социальной значимости будущей профессии, обладание высокой мотивацией к получению знаний, умений и навыков ДЛЯ успешной интеграции международное образовательное пространство естественно-научным ПО дисциплинам.
- 4. Знание научной информации, отечественного и международного опыта по профильному медицинскому направлению.

## В результате освоения курса обучаемый должен знать:

- 1. Научную терминологию и теоретические основы в соответствии с базовыми теоретическими блоками, включающими термохимию, химическое равновесие, химическую кинетику и электрохимию.
- 2. Роль и значение углубленного изучения химии на английском языке для успешного освоения будущей медицинской специальности.
- 3. Основные принципы и подходы к билингвальному переводу (английский-русский, русский-английский) научных химических текстов.

### Обучаемый должен уметь:

- 1. Производить грамотный билингвальный (английский-русский, русский-английский) устный и письменный перевод научных химических текстов в соответствии с базовыми теоретическими блоками.
- 2. Решать тестовые задания и упражнения по химии на английском языке в соответствии с углубленной программой.

- 3. Решать химические расчетные задачи и приводить письменное решение на английском языке.
- 4. Самостоятельно работать с учебной, научной и справочной литературой, эффективно ориентироваться в специализированных химических сайтах сети Интернет на английском языке.
- 5. Применять полученные при освоении образовательного курса знания, умения и практические навыки по чтению, переводу и решению заданий по химии на английском языке при овладении будущей медицинской специальностью.

# Образовательный учебный курс «Химия на английском» интегрирован со следующими учебными дисциплинами:

- 1. Английский язык.
- Физика.
- 3. Алгебра.
- 4. Геометрия.
- 5. Биология.
- 6. Информатика.

# 3. ОБЪЕМ КУРСА И ВИДЫ УЧЕБНОЙ РАБОТЫ

#### Нормативный срок обучения – 6 месяцев

№ п/п	Вид учебной работы	Трудоемкость (часы)	Примерное распределение по полугодиям*		Форма промежуточной/ итоговой аттестации	
			1	2		
			Коли	чество		
			нед	цель		
			12	13		
1	2	3	4	5	6	
1.	Тренинги по теории	6				
1.1	Теоретический блок 1 «Основы термохимии»	1	+			
1.2	Теоретический блок 2 «Химическое равновесие»	3	+			
1.3	Теоретический блок 3 «Основы химической кинетики»	1		+		

1	2	3	4	5	6
1.4	Теоретический блок 4 «Основы электрохимии»	1		+	
2.	Терминологические тренинги по теоретическим блокам	6	+	+	
3.	Тренинги по отработке навыков по интерпретации и решению заданий на английском языке	20	+	+	
4.	Прикладные тренинги по решению заданий международных экзаменов по химии на английском языке	6		+	
5.	Тестирование курса	10			
5.1	Тест-контроль 1 по теоретическому блоку «Основы термохимии»	2	+		зачет
5.2	Тест-контроль 2.1 по теоретическому блоку «Химическое равновесие»	2	+		зачет
5.3	Тест-контроль 2.2 по теоретическому блоку «Химическое равновесие»	2		+	зачет
5.4	Тест-контроль 3 по теоретическому блоку «Основы химической кинетики»	2		+	зачет
5.5	Тест-контроль 4 по теоретическому блоку «Основы электрохимии»	2		+	зачет
6.	Итоговая	2		+	экзамен
	аттестация				
Общая	трудоемкость курса	50			

<sup>\*</sup> В колонках 4-5 символом «+» отмечены полугодия для конкретного вида учебной работы.

#### 4. СОДЕРЖАНИЕ КУРСА

# І. Теоретический блок 1. Основы термохимии.

Типы термодинамических систем. Человеческий организм как термодинамическая система. Термохимические реакции. Тепловой эффект химических реакций. Энтальпия. Стандартная энтальпия химической реакции. Расчеты по термохимическим уравнениям. Стандартная энтальпия образования вещества. Стандартная энтальпия сгорания вещества. Закон Гесса. Энтальпийная диаграмма. Практическое приложение закона Гесса.

#### II. Теоретический блок 2. Химическое равновесие.

Химическое равновесие. Обратимые и необратимые химические реакции. Влияние различных факторов на смещение равновесия химических и биохимических процессов. Принцип смещения химического равновесия (принцип Ле Шателье). Практическое приложение принципа Ле Шателье. Понятие термодинамической константы равновесия. Закон действующих масс. Химическое равновесие В газовой фазе. Парциальное Анестезирующее давление. Ионные равновесия. Теории кислот и оснований. Протолитическая теория Бренстеда-Лоури. Сопряженные кислотно-основные пары. Константа кислотности, константа основности. Ионное произведение воды. Расчет рН. Степень и константа диссоциации. Закон разведения Оствальда.

#### III. Теоретический блок 3. Основы химической кинетики.

Скорость химической реакции. Факторы, влияющие на скорость химической реакции. Правило Вант-Гоффа. Теория активных столкновений. Понятие энергии активации. Энергетический профиль химической реакции. Практическое приложение основ химической кинетики к биохимическим процессам.

# IV. Теоретический блок 4. Основы электрохимии.

Окислительно-восстановительные реакции. Электронно-ионный баланс. Электролиз расплавов и растворов электролитов. Практическое приложение основ электрохимии к биохимическим процессам.

# V. Тренинги по интерпретации и решению заданий международных экзаменов по химии.

# ПРИМЕРНОЕ КАЛЕНДАРНО-ТЕМАТИЧЕСКОЕ ПЛАНИРОВАНИЕ

# Образовательного учебного курса для профильных классов медицинской направленности «ХИМИЯ НА АНГЛИЙСКОМ» для учащихся средних образовательных школ

Учебная	Тема	Тип тренинга	Количество	Вид
неделя	2	3	часов	<b>контроля</b> 5
1	<u>-</u>		4	3
TT 1	1	блок 1. Основы термохі		T
Неделя 1	Типы	Теоретический,	2	Тест-опрос
	термодинамических	терминологический.		
	систем. Человеческий			
	организм как			
	термодинамическая			
	система.			
	Термохимические			
	реакции. Тепловой			
	эффект химических			
	реакций. Энтальпия.			
	Стандартная энтальпия			
	химической реакции.			
Неделя 2	Расчеты по	Теоретический,	2	Тест-опрос
	термохимическим	терминологический.		
	уравнениям.	Отработка навыков по		
	Стандартная энтальпия	интерпретации и		
	образования вещества.	решению тестовых		
	Стандартная энтальпия	заданий и расчетных		
	сгорания вещества.	задач.		
	Закон Гесса.			
Неделя 3	Расчеты по	Терминологический.	2	Тест-опрос
	термохимическим	Отработка навыков по		
	уравнениям	интерпретации и		
	(продолжение).	решению тестовых и		
	Практическое	расчетных задач.		
	приложение закона			
	Гесса.			
Неделя 4	Тест-контроль 1 по	Контрольный.	2	Тест-
	теоретическому блоку			контроль
	«Основы термохимии».			
	Теоретический бл	пок 2. Химическое равн		
Неделя 5	Химическое равновесие.	Теоретический,	2	Тест-опрос
	Обратимые и	терминологический.		
	необратимые	Отработка навыков по		
	химические реакции.	интерпретации и		
	Влияние различных	решению тестовых		
	факторов на смещение	заданий.		
	равновесия химических			
	и биохимических			

	процессов. Принцип смещения химического равновесия (принцип Ле Шателье).			
Неделя 6	Принцип смещения химического равновесия (продолжение). Практическое приложение принципа Ле Шателье.	Терминологический. Отработка навыков по интерпретации и решению тестовых заданий.	2	Тест-опрос
Неделя 7	Понятие термодинамической константы равновесия. Закон действующих масс.	Теоретический терминологический. Отработка навыков по интерпретации и решению тестовых заданий и расчетных задач.	2	Тест-опрос
Неделя 8	Химическое равновесие в газовой фазе. Парциальное давление. Анестезирующее давление.	Теоретический терминологический. Отработка навыков по интерпретации и решению тестовых заданий и расчетных задач.	2	Тест-опрос
Неделя 9	Тест-контроль 2.1 по теоретическому блоку «Химическое равновесие».	Контрольный	2	Тест- контроль
Неделя 10	Ионные равновесия. Теории кислот и оснований. Сопряженные кислотно-основные пары.	Теоретический, терминологический. Отработка навыков по интерпретации и решению тестовых заданий.	2	Тест-опрос
Неделя 11	Ионные равновесия. Константа кислотности, константа основности. Ионное произведение воды. Расчет рН.	Теоретический, терминологический. Отработка навыков по интерпретации и решению тестовых заданий и расчетных задач.	2	Тест-опрос
Неделя 12	Степень и константа диссоциации. Закон разведения Оствальда.	Теоретический, терминологический. Отработка навыков по интерпретации и решению тестовых заданий и расчетных задач.	2	Тест-опрос
Неделя 13	Тест-контроль 2.2 по теоретическому блоку «Химическое	Контрольный	2	Тест- контроль

	равновесие».			
1	2	3	4	5
	Теоретический блок	3. Основы химической	кинетики	
Неделя 14	Скорость химической реакции. Факторы, влияющие на скорость химической реакции. Правило Вант-Гоффа.	Теоретический, терминологический. Отработка навыков по интерпретации и решению тестовых заданий и расчетных задач.	2	Тест-опрос
Неделя 15	Теория активных столкновений. Понятие энергии активации. Энергетический профиль химической реакции.	Теоретический, терминологический.	2	Тест-опрос
Неделя 16	Энергетический профиль химической реакции (продолжение). Практическое приложение правила Вант-Гоффа.	Терминологический. Отработка навыков по интерпретации и решению тестовых заданий и решению расчетных задач.	2	Тест-опрос
Неделя 17	Тест-контроль 3 по теоретическому блоку «Основы химической кинетики».	Контрольный	2	Тест- контроль
		<i>лок 4</i> . Основы электрох		
Неделя 18	Окислительно- восстановительные реакции. Электронно- ионный баланс.	Теоретический, терминологический. Отработка навыков по интерпретации и решению тестовых заданий и расчетных задач.	2	Тест-опрос
Неделя 19	Электролиз расплавов и растворов электролитов.	Теоретический, терминологический. Отработка навыков по интерпретации и решению тестовых заданий и расчетных задач.	2	Тест-опрос
Неделя 20	Электролиз расплавов и растворов электролитов (продолжение).	Теоретический, терминологический. Отработка навыков по интерпретации и решению тестовых заданий и расчетных задач.	2	Тест-опрос
Неделя 21	Тест-контроль 4 по теоретическому «Основы электрохимии».	Контрольный	2	Тест- контроль

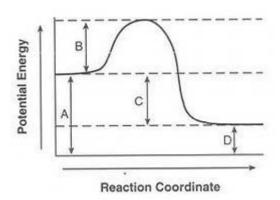
1	2	3	4	5
Неделя 22	Тренинг 1	Прикладной	2	Тренинг по
	по интерпретации и			интерпре-
	решению заданий			тации и
	международных			решению
	экзаменов по химии на			заданий
	английском языке.			
Неделя 23	Тренинг 2	Прикладной	2	Тренинг по
	по интерпретации и			интерпре-
	решению заданий			тации и
	международных			решению
	экзаменов по химии на			заданий
	английском языке.			
Неделя 24	Тренинг 3	Прикладной	2	Тренинг по
	по интерпретации и			интерпре-
	решению заданий			тации и
	международных			решению
	экзаменов по химии на			заданий
	английском языке.			
	ИТОГО	ВАЯ АТТЕСТАЦИЯ		
Неделя 25	Итоговая аттестация	Мониторинг оценки	2	Экзамен
		качества знаний		

Образцы заданий контрольных тест-блоков для полного и выборочного тренинга по научной химической терминологии, контроля эффективности усвоения знаний учащимися и оценки уровня овладения практическими навыками при чтении, интерпретации и решении заданий по химии на английском языке

- 1. At the beginning of a reaction the reaction rate for the reactants
  - (1) largest, then decreasing
  - (2) largest and remains constant
  - (3) smallest and remains constant
  - (4) smallest, then increasing
- 2. In the equilibrium reaction  $A + B \leftrightarrow AB + \text{heat}$  (in a closed container), how could the forward reaction rate be increased?
  - I. By increasing the concentration of AB
  - II. By increasing the concentration of A
  - III. By removing some of product AB
    - (A) I only
    - (B) III only
    - (C) I, II, and III
    - (D) II and III only
- 3. How many times will the rate reaction  $2A + B \rightarrow A_2B$  change if the concentration of substance A is doubled, and that of substance B is halved?

- 4. For the reaction  $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$  how will the rate of the reaction change if
  - (1) the pressure in the system is increased three times
  - (2) the volume of the system is diminished to one-third of the initial value
  - (3) the concentration of the NO is increased three times?
- 5. For the reaction of ethyl acetate alkaline hydrolysis by sodium hydroxide
  - (a) write the chemical equation and name the reaction products
  - (b) calculate the temperature coefficient value if the rate of the reaction grows 6.8 times when the temperature is increased by 30°C.
- 6. Examine the following diagram and answer the questions.

## Diagram 1.



<u>Task 1.</u>

In this graphic representation of a chemical reaction

- (1) arrow A depicts\_\_\_\_\_
- (2) arrow B depicts\_\_\_\_
- (3) arrow C depicts\_\_\_\_\_
- (4) arrow D depicts\_\_\_\_\_
- (5) arrow X depicts\_\_\_\_\_
- (A) The potential energy of the reactants
- (B) The potential energy of the products
- (C) The heat of the reaction for the forward reaction
- (D) The activation energy of the forward reaction
- (E) The activation energy of the reverse reaction

## <u>Draw the missing arrow X at the Diagram 1.</u> Task 2.

Is this reaction <u>exothermic</u> or <u>endothermic</u>? Give explanation.

7. When dissolved in water, a weak acid HA partially dissociates as shown below  $HA \Leftrightarrow H^+ + A^-$ 

The degree of dissociation,  $\alpha$ , is defined as the fraction of HA dissociated in water. The dissociation constant, Ka, is defined as the product  $[H^+][A^-]$  divided by [HA], where the brackets denote the concentrations of the respective chemical species. Give the appropriate answers to the following questions.

- (1) Setting the initial concentration of HA as  $\mathbf{c}$ , write an expression of Ka using  $\alpha$  and  $\mathbf{c}$ .
- (2) Show an expression of [H<sup>+</sup>] using Ka,  $\mathbf{c}$  and  $\mathbf{c}_{salt}$  when HA and a corresponding sodium salt NaA are dissolved together in water with initial concentration of [HA] = c and [NaA] =  $\mathbf{c}_{salt}$ . Provided that  $\mathbf{x} >> \mathbf{y}$ , you can use an approximate equation  $\mathbf{x} \pm \mathbf{y} \approx \mathbf{x}$
- 8. When dissolved in water at the concentration of 1 mol L<sup>-1</sup>, which of the substances 1) to 4) exhibits the lowest pH?
- (1) HCl

(2) HF

- (3) CH<sub>3</sub>COOH
- (4)

 $H_2S$ 

- 9. Which of the solutions 1) to 4) exhibits a pH value of 2?
- (1) 0.01 mol L<sup>-1</sup> aqueous solution of acetic acid
- (2) 0.05 mol L<sup>-1</sup> sulfuric acid
- (3) 0.01 mol L<sup>-1</sup> hydrochloric acid
- (4)  $1 \times 10^{-12}$  mol L<sup>-1</sup> aqueous solution of sodium hydroxide.
- 10. Give the appropriate name of the compound or ions for **(A)** to **(D)** below using chemical formulas. The e<sup>-</sup> denotes an electron.

The overall reaction in a fuel cell that uses KOH as electrolyte is written as follows,

$$2H_2 + O_2 \rightarrow 2H_2O$$

At the anode, (A) is oxidized by the reaction

$$(A) + 2(B) \rightarrow 2(C) + 2e^{-}$$

At the cathode, (**D**) is reduced by the reaction

(D) 
$$+2(C) + 4e^{-} \rightarrow 4(B)$$

- 11. Give the appropriate name of compounds that contain calcium for (A) to (D) by the chemical formulas.
- (i) The reaction of metallic calcium with water produces (A). (B) is obtained by the reaction of (A) with carbon dioxide.
- (ii) Oxidation of metallic calcium produces (C). The reaction of (C) with water produces (A).
- (iii) Both (A) and (B) produces (D) by their reactions with hydrogen chloride. Metallic calcium is obtained by the electrolysis of (D).

12. Give the appropriate values for (A) and (B) in the sentences below.

1 mol of graphite is completely oxidized to carbon dioxide while evolving 394 kJ of heat, and 1 mol of carbon monoxide is completely oxidized to carbon dioxide while evolving 283 kJ of heat. At 0°C, under 1 atm (**A**) L of oxygen is required to oxidize 1 mol of graphite to carbon monoxide with the heat evolution of (**B**) kJ.

#### 5. УЧЕБНО-МЕТОДИЧЕСКОЕ ОБЕСПЕЧЕНИЕ КУРСА

#### 5.1 Рекомендуемая литература

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- 2. A. Fetisova, A. Svistunov, T. Litvinova. Fundamentals of terminology, reading, interpreting and solving problems in chemistry in English. General Chemistry. Advanced Level. Workbook.-M: I.M. Sechenov First MSMU, 2016.
- (Фетисова А.Н., Свистунов А.А., Литвинова Т.М. «Основы терминологии, чтения, интерпретации и решения заданий по химии на английском языке. Общая химия. Продвинутый уровень». Рабочая тетрадь на англ.яз. -М.: ФГБОУ ВО Первый МГМУ им. И.М. Сеченова Минздрава России, 2016.)
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- Словарь химических терминов (с толкованиями, особенностями 5. употребления и английскими эквивалентами) / Под ред. В.В. Дубичинского. - Ростов н/Д: Феникс, 2006. -352 с.

#### 5.2 Средства обеспечения освоения курса

Методологическая освоения система практических навыков ориентирована на эффективное усвоение знаний и отработку умений учащихся при чтении, интерпретации и решении заданий по химии на английском языке. В этой связи запланировано представление информации с использованием когнитивной компьютерной графики, содержащей средств графические информационные экраны, демонстрационно-иллюстрирующие компьютерные модели, аудио- и видеоматериалы по химии на английском языке.

6. МАТЕРИАЛЬНО-ТЕХНИЧЕСКОЕ ОБЕСПЕЧЕНИЕ КУРСА Использование современных технологий мультимедиа.

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#### CHAPTER I

#### FUNDAMENTALS OF THERMOCHEMISTRY

Thermodynamics is the branch of science that is concerned with the transformation of energy.

Chemical thermodynamics considers the mutual conversions of various forms of energy attending chemical reaction and phase transition. Chemical thermodynamics is one of the main ways of studying chemical processes.

The main goal of chemical thermodynamics is finding solutions of the most important problems of chemical processes, namely:

- A. The quantitative determination of the energy effects attending chemical processes
- B. The establishment of whether processes can occur spontaneously under the given conditions
- C. The determination of the conditions for the spontaneous occurring of processes with a given yield of the products

#### **Basic Definitions**

For the purposes of physical chemistry, the universe is divided into two parts, **the system** and **its surroundings**. The system is the part of the world in which we have a special interest.

By a THERMODYNAMIC SYSTEM is meant any macroscopic part of the Universe being studied. This is generally an assembly of bodies conditionally separated from the surrounding world. It may be a reaction vessel, an engine, an electrochemical cell, a biological cell, and so on.

In other words, a THERMODINAMIC SYSTEM is a body or a group of bodies separated from the surroundings by an interface (boundary).

Bodies outside the confines of thermodynamic system are generalized by the term SURROUNDINGS. The surroundings are where we make our measurements.

The type of system depends on the characteristics of the boundary that divides it from the surroundings. A thermodynamic system when coming into contact with its surroundings can exchange matter and energy with them.

If matter can be transferred through the boundary between the system and its surroundings the system is classified as OPEN.

If matter cannot pass through the boundary the system classified as CLOSED. For example, a closed system can expand and thereby raise a weight in the surroundings, and it may also transfer energy to them if they are at lower temperature.

Both open and closed systems can exchange energy with their surroundings.

A thermodynamic system that can exchange neither mass nor energy with its surroundings is called ISOLATED. An isolated system is a closed system that

has neither mechanical nor thermal contact with its surroundings. Such systems do not exist in nature and they are only of theoretical importance.

A part or set of parts of a thermodynamic system having identical physical and chemical properties is called PHASE. A system consisting of one phase is HOMOGENEOUS. Examples are mixture of gases, an unsaturated solution, and a mixture of petroleum products. If a system consists of several phases separated from one another by interfaces, it is HETEROGENEOUS. Examples are a mixture of water and petroleum products, a saturated solution with an excess of salt as a precipitate, and melting ice.

The physical characteristics of a thermodynamic system (the mass, volume, temperature, pressure, composition, energy, heat capacity, surface tension are called THERMODYNAMIC PRORERTIES. The latter are divided into two groups. One of them includes the properties used to express the quantitative characteristics of a system (the mass, volume, energy, heat capacity). These properties are called EXTENSIVE. The other group combines properties used to express the qualitative characteristics of a system (the temperature, pressure, composition, density, surface tension). These properties are called INTENSIVE.

In an isolated thermodynamic system, all macroscopic changes stop with time, and the value of any of the thermodynamic properties at each point remains constant in time. The system arrives at thermodynamic equilibrium, and it is called EQUILIBRIUM one. As long as the thermodynamic properties in a system change, it remains non-equilibrium one.

In other words, a system is in EQUILIBRIUM with its surroundings when it has no tendency to undergo spontaneous change.

An adult human body is also characterized by a relative constancy of many parameters including the constancy of many biochemical variables. In fact, these are concentrations of biologically active substances. However, such a state cannot be called equilibrium since it does not apply to open systems. It is correct to say that the body is characterized by the *stationary state*. The stationary state is characterized by the constancy of parameters when the system exchanges both matter and energy with its surroundings and rate of exchange is constant.

The mass, volume, pressure, temperature, and composition of an equilibrium thermodynamic system are called the PARAMETERS of STATE.

A change in the parameters of state of a system is called a THERMODYNAMIC PROCESS.

Three thermodynamic processes are distinguished depending of which of the parameters of state remains constant during the process. They are: an ISOTHERMAL process occurring at a constant temperature of the system (T = const); an ISOBARIC process occurring at a constant pressure of the system (p = const); an ISOCHORIC process occurring at a constant volume of the system (p = const).

Neglecting insignificant temperature fluctuation in homoiothermal animals, modeling living systems can be confined to ISOBARIC-ISOTHERMAL processes occurring when both pressure and temperature are constant. Thus, the isobaric-

isothermal process in closed systems is the simplest model to describe real processes occurring in living systems.

Energy manifests itself in nature in various forms. The course of physics tells us about the kinetic and potential energies of a body moving in space relative to an observer.

Thermodynamics studies forms of energy not depending on the position of the body being studied in space. This form of energy participates in all thermodynamic processes, i.e. in mutual conversions HEAT and WORK. It was first described by the founder of theoretical thermodynamics, the well-known German physicist R. Clausius, and called INTERNAL ENERGY. It is designated by  $\boldsymbol{U}$  for a thermodynamic system as a whole.

The internal energy of a thermodynamic system is the sum of the energies of motion and interaction of the diverse particles it consists of such as molecules, ions, electrons, protons, and neutrons:

$$U = E_k + E_p + E_{ch} + E_n$$

where  $E_k$  and  $E_p$  are the kinetic and potential energies of the particles of the body,  $E_{ch}$  is the energy of interaction of the intramolecular particles of the body, and  $E_n$  is the energy of interaction of the intranuclear parts of the body.

The kinetic energy of particles is the energy of their thermal motion; it is sometimes called the *heat energy*.

The potential energy of the particles of a body characterizes their mutual attraction (internal pressure).

The energy of interaction of the intramolecular particles of a body characterizes the composition and structure of its molecules and changes only as a result of chemical transformations of the substance. This is why it is sometimes called the *chemical energy*.

The energy of interaction of the intranuclear particles of a body characterizes the composition and structure of the nuclei of its atoms and changes only in nuclear transformation of a substance. It is accordingly usually called the *nuclear energy*. The composition and structure of the nuclei of atoms in chemical transformations remain unchanged. Consequently, in all the physicochemical processes we are to study, the nuclear energy remains constant, i.e.  $E_n = \text{const.}$ 

The internal energy is a property of a system. In other words, in addition to the temperature, pressure, volume, mass, and other parameters of state, it can be used to characterize the state of a system. The internal energy is extensive property, i.e. its value depends on the amount of substance in a system. When a system consist of many parts, its internal energy equals the sum of the internal energies of the constituent parts:

$$U_{syst} = U_1 + U_2 + \dots + U_k$$

where  $U_1$ ,  $U_2$ , ...,  $U_k$  are the values of the internal energies of the 1<sup>st</sup>, 2<sup>nd</sup>, k –th parts forming the system.

Our present state of knowledge does not allow us to even approximately assess the value of the chemical and nuclear energies of substance. Hence, we cannot estimate the absolute value of the internal energy of a system. For practical purposes, it is sufficient to now the change  $(\Delta)$  in the internal energy of a system due to the change in its state, i.e. when a process occurs:

$$\Delta U = U_2 - U_1$$

where  $U_1$  and  $U_2$  are the values of the internal energy of the system in its initial and final states.

The change in the internal energy of a system occurring as a result of a process consisting of consecutive stages (the state of the system changes from the initial one through intermediate stages to the final one) equals the sum of the changes in its internal energy in the  $1^{st}$ ,  $2^{nd}$ , ..., n-th individual stages of this process:

$$\Delta U = \Delta U_1 + \Delta U_2 + \dots + \Delta U_n$$

where  $\Delta U_1$ ,  $\Delta U_2$ , ...,  $\Delta U_n$  are the changes in the internal energy of the system in the separate stages of the process.

The properties of the internal energy are summarized in the FIRST LAW of THERMODYNAMICS, otherwise known as the LAW of ENERGY CONSERVATION. It states that ENERGY CAN TRANSFORM FROM ONE FORM INTO ANOTHER, BUT IT CANNOT APPEAR OR VANISH. The total energy of an isolated system is constant.

In practical thermodynamics, it is more convenient to use more specific variants of formulation of the fist law. For example, as applied to thermomechanical systems, i.e. systems exchanging energy in the form of heat and mechanical work with their surroundings, the following variants of the law are more convenient: THE CHANGE IN THE INTERNAL ENERGY OF A SYSTEM EQUALS THE HEAT RECEIVED BY THE SYSTEM MINUS THE WORK DONE BY THE SYSTEM ON ITS SURRONDINGS:

$$\Delta U = Q - W$$

THE HEAT RECEIVED BY A SYSTEM IS SPENT ON INCREASING ITS INTERNAL ENERGY AND DOING WORK ON THE SURROUNDINGS:

$$Q = \Delta U + W$$

Here Q is the heat imparted to the system, and W is the work done by the system on its surroundings.

It should be noted that the heat received by thermodynamic system from its surroundings is assumed to be positive. The work, conversely, is assumed to be positive if it is directed from the system into the surroundings, and negative if it is directed from the surroundings into the thermodynamic system.

The change in the internal energy of a system does not depend on the path of the process, but depends only on the initial and final states of the system. This signifies that the internal energy, being a property of a system, depends on its state, i.e. is a THERMODYNAMIC FUNCTION OF STATE OF THE SYSTEM. This is one of the remarkable properties of the internal energy.

Heat and work, unlike internal energy, depend on the path of a process and characterize not a system, but a process occurring in it.

Heat and work are not energy in its direct meaning, but are forms of its transmission, i.e. energy exchange occurring between a thermodynamic system and its surroundings.

The internal energy characterizes the state of thermodynamic system and does not depend on how the system acquired the given state. Heat and work, on the other hand, characterize a thermodynamic process occurring in a system. They appear when the process begins, attend it, and stop existing when the process terminates.

The difference between heat and work lies in their physical nature.

Heat is a manifestation of the exchange of energy between particles a result of the chaotic collisions between them. The hotter particles collide with colder ones and give up a part of their kinetic energy to them, i.e. "heat" them. The latter, in turn, collide with the following colder particles, "share" their energy with them, and so on until all particles have acquired the same energy. This explains the dispersion of heat and its direction from a region with a higher temperature to one with lower temperature.

Work is the transfer of energy by moving matter. Work manifests itself in nature by a diversity of forms. For example, when a body (an assembly of particles) moves in space under the action of an applied force, mechanical work called mechanical energy is performed; when charges move in an electric field, electrical work is performed; it is called electrical energy. Radian energy, i.e. the motion of electromagnetic waves, is also a variety of work.

The external difference between heat and work consists in that the former is realized in a temperature field, and the latter in a force field. The internal energy is measured in joules (J).

Heat and work are measured in the same units as internal energy, so that they are a measure of the change in the internal energy of a system.

The heat, work, and internal energy are THERMODYNAMIC FUNCTIONS.

# Thermodynamic Functions in the Basic Reversible Processes Isochoric process.

If a system is separated from its surroundings by a rigid shell (mechanical isolation), its volume remains constant when all the other parameters of state (p, T, etc.) change.

The equation of the first law of thermodynamics ( $\Delta U = Q - W$ ) acquires the following form  $\Delta U_{\nu} = Q_{\nu}$ 

#### Isobaric process.

If a thermodynamic system is confined by a weightless movable shell, then when all the parameters of state change (V, T, etc.), the pressure in the system will equal that of the surroundings and will remain constant if the pressure in the surroundings does not change. According to the first law of thermodynamics, the heat directed into the system is spent both to change the internal energy of the system and to perform mechanical work on the surroundings  $(Q = \Delta U + W)$ 

$$Q_p = \Delta U + W_p$$

#### **ENTHALPY**

The energy of any open thermodynamic system consists of its internal energy and the additional energy appearing as a result of its introduction into another system, e.g. surroundings. This form of energy, i.e. the energy of a system exchanging both energy and matter with its surroundings, was named the ENTHALPY (from Greek enthalpein – to heat in). It is designated by the symbol  $\boldsymbol{H}$ .

The enthalpy is a more complete characteristic of the energy of a thermodynamic system. It can be used to describe both open and closed systems, whereas the internal energy is acceptable only for closed system.

Being a function of state, the enthalpy has all the properties of internal energy:

- 1. Only a single value of the enthalpy corresponds to definite state of a system.
- 2. Being an expression of the energy of a thermodynamic system, the enthalpy is an *extensive* quantity, i.e. it is proportional to the amount of substance of a system.

The enthalpy of a composite system equals the sum of the enthalpies of its constituent parts:

$$H = H_1 + H_2 + ... + H_k$$

3. A change in the enthalpy of a thermodynamic system does not depend on the path of process and characterizes only the result of a change in the state of the system:

$$\Delta H = H_2 - H_1 = (U_2 + p_2 V_2) - (U_1 + p_1 V_1) = \Delta U + p_2 V_2 - p_1 V_1$$

4. The total change in the enthalpy of a system as a result of a process consisting of n consecutive stages equals the sum of the changes of its enthalpy in all stages of the process:

$$\Delta H = \Delta H_1 + \Delta H_2 + \dots \Delta H_n$$

# Heat Effect of a Reaction

Depending on the nature of a system (of the reactants and products) a chemical process in it is attended by the absorption or evolution of heat.

If the heat of a chemical process is directed from a system into its surroundings (Q < 0), the process is EXOTHERMIC (oxidation, hydrogenetion, halogenation, polymerization, polycondensation, etc.).

If heat of the chemical process is directed from the surroundings into a system (Q > 0), the process is ENDOTHERMIC (reductation, dehydrogenation, pyrolysis, hydrolysis, etc.).

The heat of chemical process depends on the conditions under which the process occurs. In this connection, we distinguish isobaric and isochoric heat effects of a reaction. The heat of chemical process occurring at p = const and equal temperatures of the initial  $T_1$  and final  $T_2$  states of a system, i.e.  $T_1 = T_2$ , is called the *isobaric heat effect*  $Q_p$  of the relevant reaction. The heat of a chemical process occurring at V = const and  $T_1 = T_2$  is called the *isochoric heat effect*  $Q_v$  of the relevant reaction.

The isochoric heat effect of a reaction equals the change in the internal energy of the system:

$$Q_v = \Delta U$$

While the isobaric heat effect of the reaction equals the change in the enthalpy of the system:

$$Q_p = \Delta H$$

The masses of the reactants, their states of aggregation, temperature, and pressure are the most important factors influencing the heat effect of a reaction. The concept of the *standard heat effect of a reaction* has been introduced for simplifying calculations and for standardization.

The heat of a chemical process occurring at standard temperature and pressure (298 K and 101 kPa) with the formation of one mole of the product is called the standard heat effect of a reaction.

#### Hess's Law

Equations  $Q_v = \Delta U$  and  $Q_p = \Delta H$  reveal that the heat effect of a reaction has the properties of a function state because it is the heat of a process occurring under the specific conditions p = const or V = const and equal temperatures of the initial and final states of a system.

Thus signifies that the heat effect of a reaction depends on the initial and final states of a system and does not depend on its intermediate states. This conclusion, which is corollary of the fist law of thermodynamics, was made by Hess when analyzing experimental data and was named Hess's law. It states that the heat effect of a chemical reaction does not depend on the path of the reaction, i.e. on its intermediate states, but is determined only by the nature of the reactants and products and their state.

Hess's law is of a major practical and theoretical significance. It can be used to find the heat effect of any reaction without performing direct measurements.

#### Heat of Formation

To compare the characteristics of various phenomena or object, one must introduced a common "reference point" or "bench mark". This is done, for instance, when describing the altitude of a locally relative to sea level taken as reference point for measuring altitudes, or when describing the geographical longitude of a locality relative to the position of the Greenwich meridian taken as the zero one, etc. The enthalpy has to be measured in a similar way because to date there is and in the future there will be no possibility of determining its absolute value.

The enthalpy of simple substances is considered to be the same for all elementary substances in stable states of aggregation at standard temperature and pressure. It is adopted as the initial reference point for the enthalpy of a substance in chemical practice. Examples of such elementary substances are gaseous chlorine, liquid mercury, crystalline iodine, rhombic sulfur, gaseous oxygen, crystalline aluminium, graphite, and liquid bromine. One these grounds, the energies of other substances are characterized by the relevant changes in the enthalpy occurring when

they are formed from simple substances, in other words, by their heat of formation: the heat effect of the reaction of formation of one mole of a substance from the simple substances at standard temperature and pressure (298 K and 101 kPa) is called the heat of formation of the substance.

The heats of formation are given in reference books on the subject.

#### Heat of Combustion

Most organic substances are known to form carbon dioxide and water when they burn. Consequently, if we adopt the enthalpy of the combustion of products (CO<sub>2</sub> and H<sub>2</sub>O) as our initial reference point, then for thermodynamic calculations of most organic reactions we can use the relevant changes in the enthalpy occurring in the combustion of substances, or in other words, the heat of combustion: the heat of **combustion** is the heat effect of a reaction of oxidizing one mole of a substance by gaseous oxygen to its higher oxides at p = const and equal temperatures of the initial and final states of the system  $(T_1 = T_2)$ .

(The combustion of nitrogen-containing organic compounds proceeds with the formation of  $N_2$ ).

To use the heats of combustion in thermodynamic calculations, they must be standardized, i.e. converted to identical conditions: the standard heat of combustion is the heat effect of a reaction of oxidizing one mole of substances by gaseous oxygen to its higher oxides at standard temperature and pressure (298 K and 101 kPa).

#### Corollaries of Hess's Law

Hess's law has a multitude of diverse formulations that are called its corollaries. We have acquainted ourselves with one of them when considering the determination of the heat effect of an individual stage reaction. Below are given two more corollaries that are widely used in thermochemical calculations.

Calculation of the heats of reactions from the heats of formation of 1. the substances participating in them: the heat effect of a reaction equals the sum of the heats of formation of the products less the sum of the heats of formation of reactants.  $\Delta \boldsymbol{H_r}^0 = \boldsymbol{\Sigma n_j H^0}_j - \boldsymbol{\Sigma n_i H^0}_i$  where

$$\Delta H_r^0 = \Sigma n_j H_j^0 - \Sigma n_i H_i^0$$
where

 $\Delta H_r^0$  is the standard enthalpy of reaction;

 $H^0$  are the standard enthalpy values of formation of products (i) and reactants (i):

**n** are the stoichiometric numbers.

2. Calculation of the heats of reactions from the heats of combustion of the substances participating in them: the heat effect of a reaction equals the sum of the heats of combustion of the reactants less the sum of the heats of combustion of products.

$$\Delta H_r^0 = \sum n_i H_i^0 - \sum n_j H_j^0$$
where

 $\Delta H_r^0$  is the standard enthalpy of reaction;

 $\mathbf{H}^{0}$  are the standard enthalpy values of combustion of products  $(\mathbf{j})$  and reactants  $(\mathbf{i})$ ;

**n** are the stoichiometric numbers.

#### **END-OF-CHAPTER I QUESTIONS**

- 1. Classify each processes as exothermic (I) or endothermic (II):
  - (a) The burning of magnesium in air
  - (b) The crystallization of copper (II) sulfate from a saturated solution
  - (c) The thermal decomposition of magnesium nitrate
  - (d) The fermentation of glucose by yeast
  - (e) The evaporation of sea water
- 2. The energy change occurring in the chemical reaction at constant pressure is known as:
  - (a) Entropy change
  - (b) Enthalpy change
  - (c) Free energy change
  - (d) Internal energy change
- 3. Enthalpy is an expression for the
  - (a) Heat content
  - (b) Energy state
  - (c) Reaction rate
  - (d) Activation energy
- 4. The ordered form of energy transmission is:
  - (a) Internal energy
  - (b) Heat
  - (c) Work
  - $(d) \\ Enthalpy$
- 5. The disordered form of energy transmission:
  - (a) Work
  - (b) Enthalpy
  - (c) Internal energy
  - (d) Heat
- 6. The property of being able to add enthalpies is based on the
  - (a) Law of Conversation of Heat
  - (b) Fist Law of Thermodynamics
  - (c) Law of Constants

- (d) Law of  $E = mc^2$
- 7. Standard conditions (STP) are
  - (a) 0°C and 2 atm
  - (b) 32°F and 76 torr
  - (c) 273 K and 760 mm Hg
  - (d) 1°C and 7.6 cm Hg
  - (e) 0 K and 760 mm Hg
- 8. The  $\Delta H_f^o$  of a reaction is recorded for
  - (a)  $0^{\circ}$ C
  - $(b)25^{\circ}C$
  - $(c) 20^{\circ}C$
  - $(d)37^{\circ}C$
- 9. If  $\Delta H_r$  is -120 kcal, it indicates the reaction is
  - (a) Endothermic
  - (b) Exothermic
  - (c) Reversible
  - (d) Irreversible
- 10. Classify each of the following reactions as  $\Delta H_r^o$ ,  $\Delta H_f^o$ , or  $\Delta H_c^o$ :
  - (a)  $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$
  - (b) C (graphite) +  $O_2(g) \rightarrow CO_2(g)$
  - $(c) HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$
  - (d) $H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$
- 11. Calculate the  $\Delta H^{o}$  for the decomposition of methane to C(s) and diatomic gas using the following data:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g); \Delta H^o = -191.8 \text{ kJ/mol}$$

$$CO_2(g) \rightarrow C(s) + O_2(g)$$
;  $\Delta H^o = 94.0 \text{ kJ/mol}$ 

$$H_2O(g) \rightarrow H_2(g) + 1/2O_2(g); \Delta H^0 = 57.8 \text{ kJ/mol}$$

- (a) 17.8 kJ/mol
- (b) 401.4 kJ/mol
- (c) -17.8 kJ/mol
- (d) -401.4 kJ/mol
- 12. Calculate the heat of ethanol formation using the following data:

$$C_2H_5OH(1) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g); \Delta H = -327.0 \text{ kcal/mol} H_2O(g) \rightarrow H_2(g) + 1/2O_2(g); \Delta H = 68.3 \text{ kcal/mol} C(s) + O_2(g) \rightarrow CO_2(g); \Delta H = -94.1 \text{ kcal/mol}$$

- (a) -66.1 kcal/mol
- (b) 66.1 kcal/mol
- (c) 67.2 kcal/mol
- (d)-67.2 kcal/mol
- 13. The combustion of ethane produces carbon dioxide and water vapor. The balanced reaction is:

$$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$$

$$\Delta H_f^{o}(C_2H_6) = -20.2 \text{ kcal/mol}$$

$$\Delta H_f^o$$
 (CO<sub>2</sub>) = -94.1 kcal/mol

$$\Delta H_{\rm f}^{\rm o} ({\rm H_2O} ({\rm g})) = -57.8 \; {\rm kcal/mol}$$

Calculate the heat of reaction for ethane combustion, if mass of ethane is equal to 60 g.

- (a) -341.4 kcal
- (b) -254.3 kcal
- (c) -505.8 kcal
- (d) -682.8 kcal
- 14. What is the  $\Delta H^{\circ}$  value for the decomposition of sodium chlorate?

$$NaClO_3(s) \rightarrow NaCl(s) + 3/2O_2(g)$$

$$\Delta H^{o}$$
 (NaClO<sub>3</sub>(s)) = -85.7 kcal/mol

$$\Delta H^{o}(NaCl(s)) = -98.2 \text{ kcal/mol}$$

- (a) 173.9 kcal/mol
- (b)-173.9 kcal/mol
- (c) -12.5 kcal/mol
- (d) 12.5 kcal/mol
- (e) 3/2 (173.9 kcal/mol)
- 15. If 0.8 mol of NO is converted to  $NO_2$  in the following reaction, what amount of heat will be evolved?

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) + 150 \text{ kJ}$$

- (a) 30 kJ
- (b) 60 kJ
- (c) 80 kJ

- (d) 130 kJ
- (e) 150 kJ
- 16. How much heat energy is released when 8 g of hydrogen are burned? The thermal equation is  $2H_2 + O_2 \rightarrow 2H_2O + 136.64$  kcal
- (a) 68.32 kcal
- (b) 102.48 kcal
- (c) 136.64 kcal
- (d) 273.28 kcal
- (e) 546.56 kcal
- 17. How much heat is released by the following reaction  $2\text{Na}(s) + \text{Cl}_2(g) \rightarrow 2\text{NaCl}(s) + 822 \text{ kJ}$ , if 0.5 mol of sodium reacts completely with chlorine?
- (a) 205.5 kJ
- (b) 411 kJ
- (c) 822 kJ
- (d) 1644 kJ
- (e) 3288 kJ
- 18. Calculate the standard heat effect for the iron (II) sulfide formation reaction, if known that when 2.1 g of iron were combined with sulfur, 3.77 kJ are evolved.
- 19. Draw an enthalpy diagram and calculate  $\Delta H_{r}^{\, o}$  for the reaction

2Al(s) + Fe<sub>2</sub>O<sub>3</sub>(s) 
$$\rightarrow$$
 2Fe(s) + Al<sub>2</sub>O<sub>3</sub>(s)  
( $\Delta H_f^o[Al_2O_3(s)] = -1675.7 \text{ kJ/mol}; \Delta H_f^o[Fe_2O_3(s)] = -824.2 \text{ kJ/mol})$ 

20. Calculate the  $\Delta H^o$  value for the reaction of magnesium oxide dissolution in water using the following data

$$MgO(s) + 2H^{+}(aq) \rightarrow Mg^{2+}(aq) + H_2O(l); \Delta H^{o} = -145.6 \text{ kJ/mol}$$
  
 $H_2O(l) \rightarrow H^{+}(aq) + OH^{-}(aq); \Delta H^{o} = 57.5 \text{ kJ/mol}$ 

- 21. Calculate the standard enthalpy change for methane combustion reaction using the following reference values:  $\Delta H_f^o[CO_2(g)] = -393.5 \text{ kJ/mol}; \Delta H_f^o[H_2O(g)] = -241.8 \text{ kJ/mol}; \Delta H_f^o[CH_4(g)] = -74.9 \text{ kJ/mol}.$
- 22. The reduction of 12.7 g of copper (II) oxide with coal is accompanied by the release of carbon monoxide ( $\Delta H_f^o[CO(g)] = -110.5 \text{ kJ/mol}$ ) and absorption of 8.24 kJ. Calculate the standard enthalpy value of copper (II) oxide formation reaction.

- 23. Upon the complete combustion of ethylene with the formation of liquid water, 6226 kJ were evolved. Calculate the volume of oxygen that entered into the reaction under standard conditions. The standard heat of ethylene combustion reaction is equal to -1411 kJ/mol.
- 24. Calculate the value of standard enthalpy for the reactions of glucose transformation proceeding in organism:

(i) 
$$C_6H_{12}O_6(s) + O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

(ii) 
$$C_6H_{12}O_6(s) \rightarrow 2C_2H_5OH(1) + 2CO_2(g)$$

$$\Delta H_f^o [CO_2(g)] = -393.5 \text{ kJ/mol}$$

$$\Delta H_f^o [H_2O (1)] = -286.0 \text{ kJ/mol}$$

$$\Delta H_f^o [C_2 H_5 OH (1)] = -277.6 \text{ kJ/mol}$$

$$\Delta H_f^o [C_6 H_{12} O_6(s)] = -1264.0 \text{ kJ/mol}$$

Which of these reactions supplies more energy to the organism?

25. When ethanol is used as a fuel, combustion takes place as shown in the equation below

$$C_2H_5OH(1) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(1); \Delta H_c^o = -1367 \text{ kJ/mol}.$$

Calculate the standard enthalpy change of formation of ethanol using the following data

$$\Delta H_f^{o}$$
 [CO<sub>2</sub>(g)] = -393.5 kJ/mol  $\Delta H_f^{o}$  [H<sub>2</sub>O (l)] = -286.0 kJ/mol

- 26. Calculate the standard enthalpy value for ethanol formation reaction from acetaldehyde and hydrogen by thermochemical cycles, using
- (a) The standard enthalpy values of formation
- (b) The standard enthalpy values of combustion

Substance	$\Delta \mathrm{H_f^o}$ / kJ mol <sup>-1</sup>	$\Delta H_{c}^{o} / kJ \text{ mol}^{-1}$	
Ethanol (l)	-277	-1367	
Acetaldehyde (1)	-192	-1167	
Hydrogen (g)	-	-286	

Comment on two answers.

27. Give the appropriate values for (A) and (B) in the sentences below.

1 mol of graphite is completely oxidized to carbon dioxide while evolving 394 kJ of heat, and 1 mol of carbon monoxide is completely oxidized to carbon dioxide while evolving 283 kJ of heat. At 0°C, under 1 atm (**A**) L of oxygen is required to oxidize 1 mol of graphite to carbon monoxide with the heat evolution of (**B**) kJ.

#### CHAPTER II

# **CHEMICAL EQUILIBRIUM**

## **Characteristics of Equilibrium**

An equilibrium reaction has four particular features under constant conditions:

#### > It is dynamic

The phrase dynamic equilibrium means that the molecule or ions of reactants and products are continuously reacting. Reactants are continuously being changed to products and products are continuously being changed back to reactants.

#### > The forward and reverse reaction occur at the same rate

At equilibrium the rate of the forward reaction equals the rate of the backward reaction. Molecules or ions of reactants becoming products, and those in the products are becoming reactants, at the same rate.

# > The concentration of reactants and products remain constant at equilibrium

The concentrations remain constant because, at equilibrium, the rates of the forward and backward reactions are equal. The equilibrium can be approached from to directions.

#### > It requires a closed system

A closed system is one in which none of the reactants or products escapes from the reaction mixture. In an open system some matter is lost to the surroundings.

Many chemical reactions can be studied without placing them in closed containers. They can reach equilibrium in open flasks if the reaction takes place entirely in solution and no gas is lost.

#### The Law of Mass Action

The <u>Law of Mass Action</u> states that at constant temperature of a chemical system, the product of the equilibrium activities of the products raised to powers corresponding to their stoichiometric coefficients in the reaction equation divided by the product of the equilibrium activities of the reactants raised to powers corresponding to their stoichiometric coefficients is a constant quantity. It is called the <u>thermodynamic equilibrium constant</u>, Kc.

$$Kc = [\mathbf{Z}]^{z} [\mathbf{W}]^{w} / [\mathbf{X}]^{x} [\mathbf{Y}]^{y}$$

$$(xX + yY \Leftrightarrow wW + zZ)$$

#### Le Chatelier's Principle

In 1884, the French chemist H. Le Chatelier (1850-1936) formulated the **PRINCIPLE of DISPLACEMENT of EQUILIBRIUM** (now generally called the <u>Le Chatelier's Principle</u>) for the rapid qualitative determination of the direction of the shift in chemical equilibrium when the external conditions change:

if a system in stable equilibrium is subjected to a perturbation that changes any of the conditions determining the position of this equilibrium, the latter will tend to shift to counteract the effect of the perturbation.

In it <u>simplest form</u> Le Chatelier's principle is the following statement:

When a system at equilibrium is subjected to a disturbance, it responds by tending to minimize the effect of the disturbance.

#### Le Chatelier's principle for the effect of concentration

If more of a substance participating in an equilibrium being considered is added to the system, a process begins that is aimed at consuming a part of the added substance. This process will continue until equilibrium is restored. Conversely, the removal of reactant from an equilibrium system will induce processes aimed at the formation of an additional amount of this component. This is why the measures taken to increase the yield of a product include the maintaining of a high concentration of the reactants and the removal of the products formed in the course of the process.

For example,

To increase the yield of the ammonia

$$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g), \Delta H^o < 0$$
  
 $c(N_2) \text{ and } c(H_2) \uparrow$   
 $c(NH_3) \downarrow$ 

### Le Chatelier's principle for the effect of temperature

If the temperature of an equilibrium chemical system is increased (by supplying heat to it), a process begins in the system that is aimed at lowering its temperature (the absorption of heat). Conversely, if the temperature of an equilibrium system is lowered (by removing heat from it), a process begins in the system that is aimed at raising its temperature (the evolution of heat). For this reason, the yield of the products of exothermic processes ( $\Delta H < 0$ ) is increased by the conducting them at

a lower temperature, and of endothermic ones ( $\Delta H > 0$ ) by conducting them at a higher temperature.

In other words, raising the temperature of a reaction at equilibrium will shift the composition in the direction corresponding to an endothermic process.

Lowering the temperature will shift the composition in the exothermic direction.

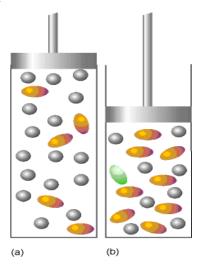
For example,

To increase the yield of the ammonia

$$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g), \Delta H^o < 0$$
 $T \downarrow$ 

#### Le Chatelier's principle for the effect of pressure

If the pressure of an equilibrium chemical system is increased, a process begins in the system that reduces the pressure in it by lowering the number of moles of the gaseous components. Conversely, if the pressure in a system is decreased, a process begins in it that raises its pressure by increasing the number of moles of the gaseous components. Hence, an increase in the pressure causes a system to alter its composition so as to reduce the pressure.



When a reaction at equilibrium is compressed (from a to b), the reaction responds by reducing the number of molecules in the gas phase.

(In this case by producing the dimers represented by the ellipses).

This is why a higher yield of the products in the processes where the number of moles of the gaseous components of the system grows, is obtained by lowering the pressure as much as possible, and in processes where the number of moles of the gaseous components of the system diminishes a higher yield is obtained by raising pressure.

For example,

To increase the yield of the ammonia

$$N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g), \Delta H^o < 0$$

$$p \uparrow$$
ACID-BASE EQUILIBRIA

There are three main concepts of acids and bases in chemistry. These are Arrhenius theory of acids and bases, Brønsted-Lowry, and Lewis theories.

Class of	Definition	Definition of Acids and Bases according to		
Substances	Arrhenius	Brønsted-Lowry	Lewis	
	Theory	Theory	Theory	
Acids	Donor of H <sup>+</sup>	Donor of H <sup>+</sup>	Acceptor of an electron pairs	
Bases	Donor of OH	Acceptor of H <sup>+</sup>	Donor of an electron pairs	

To describe reactions accompanied by changes in the acid-base properties of reactants modern chemistry uses the theory of acids and bases developed by Danish chemist J. N. Brønsted and the English chemist T.M. Lowry in 1923.

The Brønsted-Lowry classification of acids and bases

A Brønsted acid, HA, is a proton donor.

$$HA(aq) + H2O(1) \Leftrightarrow H3O+(aq) + A-(aq)$$

A Brønsted base, B, is a proton acceptor.

$$B (aq) + H_2O (l) \Leftrightarrow HB^+ (aq) + OH^-(aq)$$

#### Conjugate base

The conjugate base of an acid **HA** is the base **A** formed proton loss from the acid HA.

HA (aq) + H<sub>2</sub>O (l) 
$$\Leftrightarrow$$
 H<sub>3</sub>O<sup>+</sup> (aq) + A<sup>-</sup> (aq)

a

CH<sub>3</sub>COOH + H<sub>2</sub>O  $\Leftrightarrow$  H<sub>3</sub>O<sup>+</sup> + CH<sub>3</sub>COO<sup>-</sup>

a

b

1

#### Conjugate acid

The conjugate acid of a base  $\bf B$  is the acid  $\bf BH^+$  formed by proton transfer to the base.

B (aq) + H<sub>2</sub>O (l) 
$$\Leftrightarrow$$
 HB<sup>+</sup> (aq) + OH<sup>-</sup> (aq)

b<sub>1</sub> \_\_\_\_\_\_a

NH<sub>3</sub> + H<sub>2</sub>O  $\Leftrightarrow$  NH<sub>4</sub><sup>+</sup> + OH<sup>-</sup>

b<sub>1</sub> \_\_\_\_\_a

CH<sub>3</sub>COOH + H<sub>2</sub>O  $\Leftrightarrow$  H<sub>3</sub>O<sup>+</sup> + CH<sub>3</sub>COO<sup>-</sup>

b<sub>2</sub> \_\_\_\_a

The equilibrium system of undissociated acid and conjugate base or undissociated base and conjugate acid being referred to as a conjugate acid-base pair.

Molecules and ions able to interact both with acids and bases are called ampholytes.

The strength of acids is determined by their ability to donate a proton, and that of bases by their ability to accept it. The measure of this ability is the <u>acidity constant</u> in relation to acid and the <u>basicity constant</u> in relation to base.

# **Acidity Constant**

The acidity constant,  $\mathbf{K}_{a}$ , of an acid (including the conjugate acid of a base) is a measure of the proton-donating strength of the acid to water. It is defined as follows

HA (aq) + H<sub>2</sub>O (l) 
$$\Leftrightarrow$$
 H<sub>3</sub>O<sup>+</sup>(aq) + A<sup>-</sup> (aq)  
 $\mathbf{K_a} = [\mathbf{H_3O^+}] [\mathbf{A^-}] / [\mathbf{HA}]$ 

Acidity constants are also termed "acid ionization constants" and (less appropriately) "dissociation constants".

# The significance of pKa

It is common to report acidity constants as their negative logarithms in the form

$$pK_a = -logK_a$$

Note that the lager the value of  $pK_a$  the weaker the acid.

#### **Basicity Constant**

The basicity constant,  $\mathbf{K}_{\mathbf{b}}$ , of a Brønsted base is a measure of its ability to accept a proton from water.

It is defined as follows

B (aq) + H<sub>2</sub>O (l) 
$$\Leftrightarrow$$
 HB<sup>+</sup>(aq) + OH<sup>-</sup>(aq)  
 $\mathbf{K_b} = [\mathbf{HB^+}] [\mathbf{OH^-}] / [\mathbf{B}]$ 

Basicity constants are also termed "base ionization constants" and (less appropriately) "dissociation constants".

# The significance of pK<sub>b</sub>

It is common to report bacisity constants as their negative logarithms in the form

$$pK_b = - logK_b$$

Note that the lager the value of  $pK_b$  the weaker the base.

#### The relation between K<sub>a</sub> and K<sub>b</sub>

In modern work, it is rare to employ and report the basicity constant itself. Instead, the strength of the base is expressed in terms of the acidity constant of conjugate acid of the base (that is, in terms of the  $pK_a$  of the acid  $HB^+$ ).

The two quantities are related by

$$p\mathbf{K}_a + p\mathbf{K}_b = p\mathbf{K}_w$$

alternatively

$$\mathbf{K}_a\mathbf{K}_b=\mathbf{K}_w$$

where  $K_w$  is the <u>ion product of water</u>. It follows that <u>the larger the  $pK_{\underline{a}}$  of the</u> conjugate acid, the stronger the base.

# The pH of a Solution

The formal definition of the pH is

$$pH = -\log a(H^+)$$

where a(H<sup>+</sup>) is the activity of the hydrogen ions in the solution.

The pH of pure water is 7.0 at  $25^{\circ}$ C, and this value corresponds to a neutral solution at this temperature; pH > 7 corresponds to a basic solution and pH < 7 corresponds to an acidic solution.

#### The relation between pH and pOH

The quantity pOH is sometimes encountered

$$pOH = -log \ a(OH^{-}).$$

A convenient relation is  $pH + pOH = pK_w$ 

where K<sub>w</sub> is the ion product of water.

#### **Dissociation of Water**

Water molecules have a limited tendency to dissociate (ionize) into H<sup>+</sup> and OH<sup>-</sup>

$$H_2O \Leftrightarrow H^+ + OH^-$$

Note that the dissociation is reversible.

The tendency of water dissociate is given by

$$K = [H^{+}][OH^{-}]/[H_{2}O]$$

Where the terms in brackets represent concentrations of hydrogen ions, hydroxyl ions, and undissociated water molecules at equilibrium; that is when the rate of the forward reaction (dissociation) equals the rate of the backward reaction (association) and K is the equilibrium constant, or the dissociation constant of water.

At 25°C, the value of  $K_d$  is  $1.8 \times 10^{-16}$ .

#### **Ion Product of Water**

Since undissociated water is present in great excess, its concentration is virtually constant (55.56 mol).

(The molar mass of water equals 18 g mol<sup>-1</sup>; therefore, in 1 L, or 1000 g, there is 1000/18 mol of water).

$$[H_2O] = 55.56 \text{ mol}$$
 $K = [H^+] [OH^-] / [H_2O]$ 
 $1.8 \times 10^{-16} = [H^+] [OH^-] / 55.56$ 
 $1 \times 10^{-14} = [H^+] [OH^-] = K_w$ 

This constant value for the concentration of water can be incorporated into the dissociation constant to give a new constant, the so-called <u>ion product of water</u>, or  $K_w$ 

$$K_{w} = [H^{+}] [OH^{-}]$$

At 25°C,

$$K_w = 1 \times 10^{-14}$$

It is important to realize that the ion product of water is constant for all aqueous solutions, even those contain dissolved acids (proton donors) or dissolved bases (proton acceptors).

- ➤ If a larger number of hydrogen ions (protons) are added to pure water, the concentration of OH ions must decrease in order that the ion product of water will remain 10<sup>-14</sup> at 25°C.
- ➤ Conversely, if a larger number of hydroxyl ions are added, the concentration of protons will have to decrease.

#### SOLUTIONS OF ELECTROLYTES

#### **Degree of Dissociation and Dissociation Constant**

Electrolytes are substances whose solutions conduct an electric current.

Electrolytes in solutions dissociate into ions, which was indicated in the hypothesis of electrolytic dissociation (1887) advanced by Arrhenius. This phenomenon is characterized by the <u>degree of dissociation</u>  $\alpha$ , which is the ratio of the number of solute molecules:

$$\alpha = \frac{N_d}{N_{tot}}$$

Depending on the value of  $\alpha$ , electrolytes are divided into weak ones ( $\alpha$ <0.05), strong ones ( $\alpha$ >0.3), and ones of moderate strength (0.05< $\alpha$ <0.3).

The dissociation of molecules into ions is a reversible process controlled by the second law of thermodynamics, i.e. it can be considered as a variety of chemical equilibrium. Consequently, the <u>dissociation constant</u>  $\mathbf{K_d}$  has been introduced to characterize electrolytic dissociation more completely. It is the equilibrium constant of this process. If the compound AB dissociates according to the scheme

$$AB \rightarrow A^+ + B^-$$

then

$$\mathbf{K}_{\mathbf{d}} = [\mathbf{A}^{+}] [\mathbf{B}^{-}] / [\mathbf{A}\mathbf{B}]$$

where [A<sup>+</sup>], [B<sup>-</sup>], and [AB] are the equilibrium concentrations of the cations, anions, and undissociated molecules.

The following relation, known as <u>Ostwald's Dilution Law,</u> exists between  $\mathbf{K}_d$  and  $\alpha$ 

$$\mathbf{K_d} = \frac{C\alpha^2}{1-\alpha}$$

The dissociation constant  $K_d$ , being an equilibrium constant, depends on the nature of the system and the temperature, but does not depend on the concentration of a substance. This means that the degree of dissociation  $\alpha$  depends on the concentration of the electrolyte.

For weak electrolytes with  $\alpha << 1$ , we can write

$$\mathbf{K}_{d} \approx \mathbf{c}\alpha^{2} \ or \ \alpha \approx \sqrt{\frac{K_{d}}{C}}$$

# **EQUILIBRIA IN GAS REACTIONS**

For reactions involving mixture of gases, it is easier to measure the pressure than to measure concentrations. The total pressure in a mixture of gases is due to each molecule bombarding the walls of the container. At constant temperature, each gas in the mixture contributes to the total pressure in proportion to the number of moles. The pressure exerted by any one gas in the mixture is calls its *partial pressure*.

The total pressure of a gas equals the sum of the partial pressures of the individual gases.

$$\mathbf{p}_{\text{total}} = \mathbf{p}_{\text{A}} + \mathbf{p}_{\text{B}} + \mathbf{p}_{\text{C}} + \dots$$
where

 $p_A$ ,  $p_B$ ,  $p_C$  are the partial pressures of the individual gases in the mixture.

# Equilibrium expressions involving partial pressures

We write equilibrium expressions in terms of partial pressures in a similar way to equilibrium expression in terms of concentrations.

For example, the equilibrium expression for the reaction

$$2SO_2(g) + O_2(g) \Leftrightarrow 2SO_3(g)$$
  
is written as  $\mathbf{K_p} = \mathbf{p^2}_{SO3} / \mathbf{p^2}_{SO2} \times \mathbf{p_{O2}}$ 

<u>Anesthetic pressure</u> is the partial pressure of anesthetic gas needed to achieve the effect of anesthesia.

# **END-OF-CHAPTER II QUESTIONS**

- 1. In which system the increasing of pressure will cause of the shifting equilibrium to the right?
  - (a)  $2HI(g) \Leftrightarrow H_2(g) + I_2(g)$
  - (b)  $C(s) + S_2(g) \Leftrightarrow CS_2(g)$
  - $(c) C_3H_6(g) + H_2(g) \Leftrightarrow C_3H_8(g)$
  - $(d)H_2(g)+F_2(g){\Leftrightarrow}2HF(g)$
- 2. In which system the increasing of pressure will cause of the shifting equilibrium to the left?
  - $\text{(a) } N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g) + Q$
  - $(b) N_2O_4(g) \Leftrightarrow 2NO_2(g) Q$
  - $(c) CO_2(g) + H_2(g) \Leftrightarrow CO(g) + H_2O(g) Q$
  - $(d)4HCl(g)+O_2(g){\Leftrightarrow}2H_2O(g)+2Cl_2(g)+Q$
- 3. In which system the increasing of pressure and decreasing of temperature will cause of the shifting reaction equilibrium towards the products formation?
  - $(a)\,N_2(g) + 3H_2(g) {\Longleftrightarrow} 2NH_3(g) + Q$
  - $(b)\,N_2(g) + O_2(g) {\Longleftrightarrow} 2NO(g) Q$
  - $(c) \operatorname{Cl}_2(g) + \operatorname{H}_2(g) \Leftrightarrow 2\operatorname{HCl}(g) + Q$
  - $(d)C_2H_2(g){\Leftrightarrow}2C(s)+H_2(g)-Q$
- 4. In which system the increasing of hydrogen concentration will cause of the shifting reaction equilibrium towards the reactants formation?
  - $(a) C(s) + 2H_2(g) \Leftrightarrow CH_4(g)$
  - $(b)2NH_3(g) \Leftrightarrow N_2(g) + 3H_2(g)$
  - $(c) 2H_2(g) + O_2(g) \Leftrightarrow 2H_2O(g)$
  - $(d) FeO(s) + H_2(g) \Leftrightarrow Fe(s) + H_2O(g)$
- 5. Chemical equilibrium of the endothermic reaction  $2PCl_3(g) \Leftrightarrow 3Cl_2(g) + 2P(s)$  will shift to the right if
  - (a) concentration of chlorine will increase
  - (b) concentration of PCl<sub>3</sub> will decrease
  - (c) pressure will increase
  - (d) temperature will increase
  - (e) temperature will decrease

- 6. What would be the change of temperature and pressure for shift chemical equilibrium of exothermic reaction  $2SO_2(g) + O_2(g) \Leftrightarrow 2SO_3(g)$  to formation of sulfur (VI) oxide?
  - (a) elevation of temperature and depression of pressure
  - (b) depression both temperature and pressure
  - (c) elevation both temperature and pressure
  - (d) depression of temperature and elevation of pressure
  - (e) no change both temperature and pressure
- 7. For the reaction

$$CH_3COOH(1) + C_2H_5OH(1) \Leftrightarrow CH_3COOC_2H_5(1) + H_2O(1)$$
 explain what happens to the position of equilibrium when:

- (a) more ethyl ethanoate is added
- (b) some ethanol is removed
- 8. For the reaction

$$Ce^{4+}(aq) + Fe^{2+}(aq) \Leftrightarrow Ce^{3+}(aq) + Fe^{3+}(aq)$$

explain what happens to the position of equilibrium when:

- (a) the concentration of Fe<sup>2+</sup>(aq) ions is increased
- (b) water is added to the equilibrium mixture
- 9. Predict the effect of increasing the pressure on the reaction  $N_2O_4(g) \Leftrightarrow 2NO_2(g)$
- 10. Predict the effect of increasing the pressure on the reaction  $CaCO_3(s) \Leftrightarrow CaO(s) + CO_2(g)$
- 11. Predict the effect of decreasing the pressure on the reaction  $2NO_2(g) \Leftrightarrow 2NO(g) + O_2(g)$
- 12. Predict the effect of increasing the temperature on the reaction:

$$H_2(g) + CO_2(g) \Leftrightarrow H_2O(g) + CO(g) \Delta H_r = +41.2 \text{ kJ/mol}$$

13. In the reaction

$$Ag_2CO_3(s) \Leftrightarrow Ag_2O(s) + CO_2(s)$$

Increasing the temperature increases the amount of carbon dioxide formed at constant pressure. Is this reaction exothermic or endothermic? Explain your answer.

14. Write equilibrium expression for the reaction

$$CO(g) + 2H_2(g) \Leftrightarrow CH_3OH(g)$$

- 15. Write equilibrium expression for the reaction  $4HCl(g) + O_2(g) \Leftrightarrow 2H_2O(g) + 2Cl_2(g)$
- 16. Write an expression for Kc  $N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$
- 17. Write an expression for Kc  $2SO_2(g) + O_2(g) \Leftrightarrow 2SO_3(g)$
- 18. Ethanol reacts with ethanoic acid to form ethyl ethanoate and water.  $500 \text{ cm}^3$  of the reaction mixture contained 0.235 mol of ethanoic acid and 0.035 mol of ethanol together with 0.182 mol of ethyl ethanoate and 0.182 mol of water. Use this data to calculate a value of  $K_c$  for this reaction.
- 19. Propanone reacts with hydrogen cyanide as follows:

 $CH_3COCH_3 + HCN \Leftrightarrow CH_3C(OH)(CN)CH_3$ 

A mixture of  $0.0500 \text{ mol } L^{-1}$  propanone and  $0.0500 \text{ mol } L^{-1}$  hydrogen cyanide is left to reach equilibrium at room temperature. At equilibrium the concentration of the product is  $0.0233 \text{ mol } L^{-1}$ . Calculate  $K_c$  of this reaction.

20. Calculate the value of Kc for the following reaction

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

It is known, that initial concentration of hydrogen is equal to 10.00 mol L<sup>-1</sup>, and the same for carbon dioxide. The equilibrium concentration value of carbon monoxide is equal to 9.47 mol L<sup>-1</sup>.

- 21. Identify the acid and the base on the right-hand side of the equilibrium  $HClO_2 + HCOOH \Leftrightarrow ClO_2^- + HCOOH_2^+$
- 22. Identify the acid and the base on the right-hand side of the equilibrium  $H_2S + H_2O \Leftrightarrow HS^- + H_3O^+$
- 23. Identify the acid on the right-hand side of this equation which is conjugate with the base on the left-hand side

 $CH_3NH_2 + H_2O \Leftrightarrow CH_3NH_3^+ + OH^-$ 

24. Identify the acid on the right-hand side of this equation which is conjugate with the base on the left-hand side

 $CH_3COOH + H_2O \Leftrightarrow H_3O^+ + CH_3COO^-$ 

25. Identify the acid on the right-hand side of this equation which is conjugate with the base on the left-hand side

 $NH_2CH_2COOH + OH^- \Leftrightarrow NH_2CH_2COO^- + H_2O$ 

26. Identify the base on the right-hand side of this equation which is conjugate with the acid on the left-hand side

$$NH_2CH_2COOH + OH^- \Leftrightarrow NH_2CH_2COO^- + H_2O$$

27. Identify the base on the right-hand side of this equation which is conjugate with the acid on the left-hand side

$$NH_2CH_2COOH + H_3O^+ \Leftrightarrow H_3N^{\oplus}CH_2COOH + H_2O$$

28. Identify the acid on the right-hand side of this equation which is conjugate with the base on the left-hand side

$$NH_2CH_2COOH + H_3O^+ \Leftrightarrow H_3N^{\oplus}CH_2COOH + H_2O$$

- 29. Both hydrochloric acid and ethanoic acid react with magnesium. The rate of reaction of 1.0 mol L<sup>-1</sup> hydrochloric acid with magnesium is much faster than the rate of reaction of 1.0 mol L<sup>-1</sup> ethanoic acid. Explain why.
- 30. Choose the correct relationship between acidity constant and basicity constant:
  - (a)  $pK_a + pK_b = pK_w$
  - (b)  $K_a/K_b = K_w$
  - (c)  $K_aK_b = K_w$
  - $(d) K_a K_b = K_w^2$
  - $(e) pK_a pK_b = K_w$
- 31. When dissolved in water at the concentration of 1 mol L<sup>-1</sup>, which of the substances a) to d) exhibits the lowest pH?
  - (a) hydrochloric acid
  - (b) hydrofluoric acid
  - (c) ethanoic acid
  - (d) hydrogen sulfide
- 32. Which of the solutions a) to d) exhibits a pH value of 2?
- (a) 0.01 mol L<sup>-1</sup> aqueous solution of acetic acid
- (b) 0.05 mol L<sup>-1</sup> sulfuric acid
- (c) 0.01 mol L<sup>-1</sup> hydrochloric acid
- (d)  $1 \times 10^{-12}$  mol L<sup>-1</sup> aqueous solution of sodium hydroxide.
- 33. When dissolved in water, a weak acid HA partially dissociates as shown below

$$HA \Leftrightarrow H^+ + A^-$$

The degree of dissociation,  $\alpha$ , is defined as the fraction of HA dissociated in water. The dissociation constant, Ka, is defined as the product  $[H^+][A^-]$  divided by [HA], where the brackets denote the concentrations of the respective chemical species. Give the appropriate answers to the following questions.

- (a) Setting the initial concentration of HA as  $\mathbf{c}$ , write an expression of Ka using  $\alpha$  and  $\mathbf{c}$ .
- (b) Show an expression of  $[H^+]$  using Ka,  $\mathbf{c}$  and  $\mathbf{c}_{salt}$  when HA and a corresponding sodium salt NaA are dissolved together in water with initial concentration of  $[HA] = \mathbf{c}$  and  $[NaA] = \mathbf{c}_{salt}$ . Provided that  $\mathbf{x} >> \mathbf{y}$ , you can use an approximate equation  $\mathbf{x} \pm \mathbf{y} \approx \mathbf{x}$
- 34. The reaction below was carried out at a pressure 100.0 kPa and at constant temperature

$$N_2(g) + O_2(g) \Leftrightarrow 2NO(g)$$

The partial pressure of nitrogen and oxygen are both 48.5 kPa. Calculate the partial pressure of the nitrogen (II) oxide at equilibrium.

35. In the reaction

$$2SO_2(g) + O_2(g) \Leftrightarrow 2SO_3(g)$$

the equilibrium partial pressures at constant temperature for sulfur (IV) oxide, sulfur (VI) oxide, and oxygen are equal to  $1.0 \times 10^3$  kPa,  $8.0 \times 10^3$  kPa,  $7.0 \times 10^3$  kPa, respectively.

Calculate the value of Kp for this reaction.

36. Nitrogen reacts with hydrogen to form ammonia. The pressure exerted by the mixture of hydrogen, nitrogen and ammonia is  $2.00 \times 10^4$  kPa. Under these conditions the partial pressure of nitrogen is  $1.49 \times 10^4$  kPa and the partial pressure of hydrogen is  $0.40 \times 10^4$  kPa. Calculate the value of Kp for the ammonia formation reaction.

#### CHAPTER III

#### FUNDAMENTALS OF CHEMICAL KINETICS

#### **Basic Definitions**

A chemical reaction is a change in the form of existence of matter. For example, a mixture of hydrogen with oxygen transforms into water, isoprene into rubber, etc. A chemical processes on a molecular level is a change in the structure, and in the majority of cases also decomposition of the molecules as a result of their interaction.

Single interactions (collisions) of molecules leading to the formation of new particles are called *elementary events* of a chemical reaction. In accordance with the number of molecules participating in elementary event, we distinguish uni-, bi-, and trimolecular reactions. A reaction in which the number of reacting molecules is more than three has a low probability and does not practically occur.

Any chemical reaction consists of an infinitely large number of elementary events. If a reaction consists of a multitude of identical elementary events, it is said to be a *single-stage* or elementary one.

*Molecularuty* is the number of molecules coming together to react in an elementary reaction.

An elementary reaction is a single step in a (possibly) multi-step reaction mechanism.

An elementary reaction is classified as unimolecular if it involves only a single reactant molecule  $(A \Rightarrow B)$ .

An elementary reaction is classified as bimolecular if two reactant molecules are involved (A + B  $\Rightarrow$  C).

Sometimes a reaction is a set of diverse alternating or simultaneously occurring elementary events. In these cases, the chemical reaction is said to be <u>complex</u> (multistage).

The set of stages that a chemical reaction consists of is called the *mechanism of the reaction*.

A chemical transformation in a homogeneous system is called a homogeneous chemical reaction (examples are reactions in solutions, melts, or gases). A chemical transformation in a heterogeneous system is called a heterogeneous chemical reaction (examples are the formation or dissolving of precipitates, polymerization).

Let us the first consider one of the most important characteristics of chemical processes, namely, the <u>rate of reaction</u>. The latter determines the real possibility of the proceeding of a reaction that has been "allowed" by thermodynamics.

#### The Definition of Rate

The <u>rate of chemical reaction</u> is measured by the amount of substance entering into the reaction or formed in the reaction in unit time and in unit volume of the system (for a homogeneous reaction) or on unit surface area of a phase interface (for heterogeneous reaction).

For a homogeneous process occurring at constant volume, the rate of a reaction can also be determined through the changes in the concentrations of the reactants or products.

The rate of homogeneous chemical reaction (in gases and solutions) is measured by the change in the concentration of one of the reactants or products occurring in unit time.

Since the rate of a reaction changes continuously in the course of the process, it is usually expressed by the first derivative of the concentration of the reactants with respect to time:

$$rate = \frac{dC_{pr}}{dt} \qquad \text{or} \quad rate = -\frac{dC_{r}}{dt}$$

The signs in the right-hand sides of these equations are different because in the course of a reaction the concentration of the reactants diminish, and those of the products grow.

In general case, we can write:

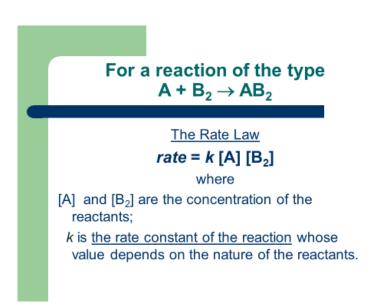
$$rate = \left| \frac{dC}{dt} \right|$$

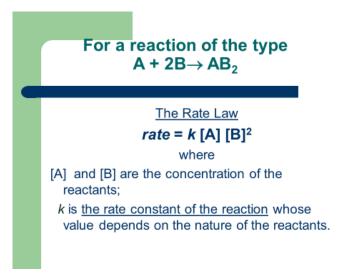
The rate of a reaction depends on many factors such as the temperature, pressure, concentration of the reactants, chemical nature of the process, the presence of impurities, and the nature of the medium in which the process is going on, the presence of catalysts in the system.

At a constant temperature, the rate in a specific chemical system depends only on the concentration of the reactants. The mathematical form showing how the rate of a chemical reaction depends on the concentration of the reactants is called a <u>kinetic equation</u>. It is very important to note that the kinetic equation is concerned with the nature of the process within the interval between its beginning and end. For this reason, even reactions whose general form is of the same type can be describe by different kinetic equations.

When the collisions of two reacting particles is needed for a reaction to occur, the dependence of the reaction rate on the concentrations is determined by the Law of Mass Action: at a constant temperature, the rate of a chemical reaction is directly proportional to the product of the concentration of the reactants (*The Fundamental Law of Chemical Kinetics or the Rate Law*).

#### **Rate Law**

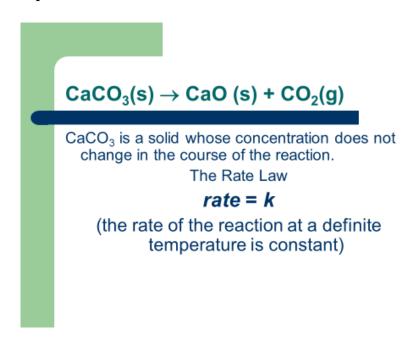




The simultaneous collision of more than three particles is extremely improbable. Consequently, reactions whose equations include a great number of particles proceed in several steps, each of which occurs because of the collisions of

two (less frequently, three) particles. In such cases, the law of mass action can be applied to the individual steps of a process, but not to a reaction as a whole.

In heterogeneous reactions, the concentrations of the substances in the solid phase do not usually change in the course of a reaction, and for this reason they are not included in the equation of the law of mass action.



The *rate constant of a reaction* is the constant of proportionality between the rate of the reaction and the concentrations of the species taking part in the reaction.

The rate constant of the reaction, k, depends on the nature of reactants, the temperature, and also on the nature of the substances in the system that do not participate in its thermodynamic changes.

The physical meaning of the rate constant comes to light when we consider the rate of a reaction with a concentration of the reactants equal to unity.

# The Physical Meaning of the Rate Constant k equals a rate of a reaction at reactant concentrations equal to unity (1 mol/L): $rate = k \cdot 1 = k$

In other words, k equals a rate of a reaction at reactant concentrations equal to unity.

#### Van't Hoff's Rule

The temperature dependence of the rate of a reaction (or the rate constant of a reaction) can be expressed by the equation

$$\frac{K_{T+\Delta T}}{K_{T}} = \gamma^{\frac{\Delta T}{10}}$$

 $\gamma$  is the temperature coefficient of the reaction rate whose value for most reactions ranges from 2 to 4.

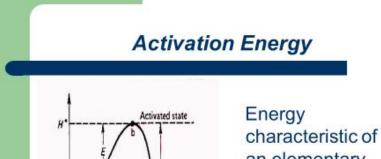
#### Activation Energy

The <u>activation energy</u> of a chemical reaction is the parameter that governs the temperature-dependence of its rate.

In collision theory, the activation energy is identified with the minimum kinetic energy along the line centers of two colliding reactant molecules.

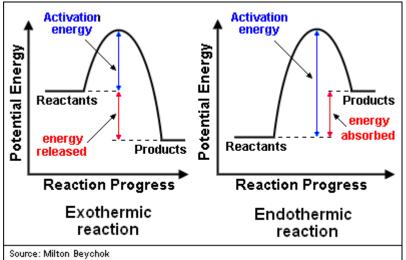
<u>Collision theory</u> is an interpretation of the rates of bimolecular elementary reactions in the gas phase in terms of a model in which reaction occurs when two molecules collide provided that they possess at lest a minimum kinetic energy along their line of centers.

In solution, the activation energy is more a complex quantity, but is nevertheless still to be identified with the height of the energy barrier along the reaction coordinate.



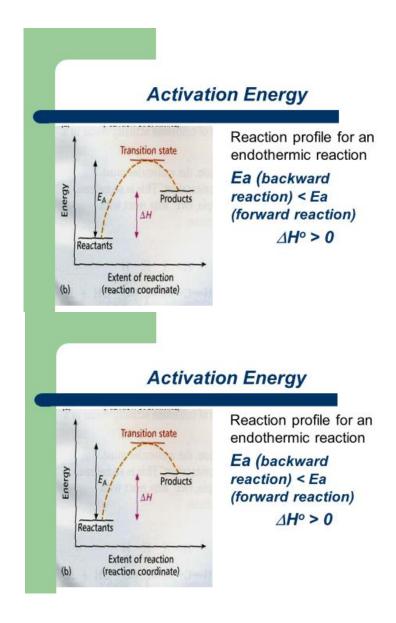
Reaction coordinate

an elementary reaction event Final state



Enthalpy H

Energy level diagrams of exothermic and endothermic reactions.  $^{[4][5][6]}$ 



# **END-OF-CHAPTER III QUESTIONS**

- 1. At the beginning of a reaction, the reaction rate for the reactants
  - (a) largest, then decreasing
  - (b) largest and remains constant
  - (c) smallest and remains constant
  - (d) smallest, then increasing
- 2. The reaction rate law applied to the reaction  $aA + bB \rightarrow AB$  gives the expression
  - (a) rate =  $k [A]^b [B]^a$
  - (b) rate =  $k [A]^{a} [B]^{b}$
  - (c) rate =  $k [AB]^a [A]^b$
  - (d) rate =  $k [B]^a [AB]^b$

- 3. If a reaction proceeds in several steps, the elementary process with the highest activation energy is known as the:
  - (a) Transition step
  - (b) Favorable step
  - (c) Rate-determining step
  - (d) Activated complex step
- 4. Which one is NOT an important condition for a chemical reaction?
- (a) The reacting molecules are in the correct orientation to one another
- (b) The molecules have enough energy to react once they have collided
- (c) The molecules must make contact
- (d) None of the above
- 5. In the equilibrium reaction  $A + B \leftrightarrow AB + \text{heat}$  (in a closed container), how could the forward reaction rate be increased?
  - I. By increasing the concentration of AB
  - II. By increasing the concentration of A
  - III. By removing some of product AB
  - (a) I only
  - (b) III only
  - (c) I, II, and III
  - (d) II and III only
- 6. How many times will the rate reaction  $2A + B \rightarrow A_2B$  change if the concentration of substance A is doubled, and that of substance B is halved?
- 7. For the reaction  $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$  how will the rate of the reaction change if the pressure in the system is increased three times?
- 8. For the reaction  $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$  how will the rate of the reaction change if the volume of the system is diminished to one-third of the initial value?
- 9. For the reaction  $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$  how will the rate of the reaction change if the concentration of the NO is increased three times?
- 10. How will the rate of the reaction  $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$  change if the volume of the reaction vessel is doubled?
- 11. How many times must the concentration of substances  $B_2$  in the system  $2A_2(g) + B_2(g) \rightarrow 2A_2B(g)$  be increased for the rate of the forward reaction to remain unchanged when the concentration of substance A is lowered to one-fourth of its initial value?

- 12. Industrially, phosgene is produced by passing purified <u>carbon monoxide</u> and <u>chlorine</u> gas through a bed of porous <u>activated carbon</u>, which serves as a <u>catalyst</u>. It is known that the concentration of carbon monoxide in the system was increased from 0.03 to 0.12 mol L<sup>-1</sup>, and that of the chlorine from 0.02 to 0.06 mol L<sup>-1</sup>. How many times did the rate of the forward reaction increase?
- 13. Calculate the temperature coefficient value if the rate of the reaction grows 6.8 times when the temperature is increased by 30°C.

Questions 14-22 refer to the Diagram 1

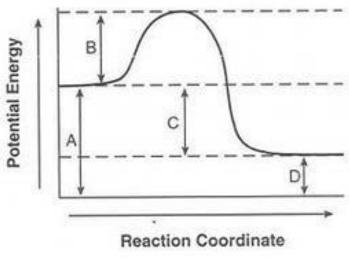


Diagram 1

- 14. In this graphic representation of a chemical reaction arrow A depicts
  - (a) The potential energy of the reactants
  - (b) The potential energy of the products
  - (c) The heat of the reaction for the forward reaction
  - (d) The activation energy of the forward reaction
  - (e) The activation energy of the reverse reaction
- 15. In this graphic representation of a chemical reaction arrow B depicts
  - (a) The potential energy of the reactants
  - (b) The potential energy of the products
  - (c) The heat of the reaction for the forward reaction
  - (d) The activation energy of the forward reaction
  - (e) The activation energy of the reverse reaction

- 16. In this graphic representation of a chemical reaction arrow C depicts
  (a) The potential energy of the reactants(b) The potential energy of the products(c) The heat of the reaction for the forward reaction(d) The activation energy of the forward reaction
- 17. In this graphic representation of a chemical reaction arrow D depicts
  - (a) The potential energy of the reactants
  - (b) The potential energy of the products
  - (c) The heat of the reaction for the forward reaction
  - (d) The activation energy of the forward reaction

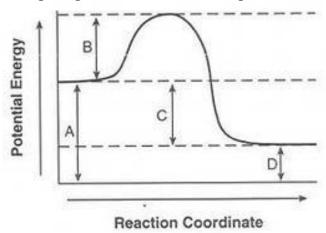
(e) The activation energy of the reverse reaction

- (e) The activation energy of the reverse reaction
- 18. In this graphic representation of a chemical reaction the activation energy of the reverse reaction is
  - (a) Arrow A + arrow C
  - (b) Arrow A + arrow D
  - (c) Arrow B + arrow A
  - (d)Arrow B + arrow C
  - (e) Arrow A + arrow B + arrow C
- 19. In this graphic representation of a chemical reaction, which arrow depicts the activation energy of the forward reaction?
  - (a) Arrow A
  - (b) Arrow B
  - (c) Arrow C
  - (d) Arrow D
- 20. In this graphic representation of a chemical reaction, which arrow depicts the potential energy of the reactants?
  - (a) Arrow A
  - (b) Arrow B
  - (c) Arrow C
  - (d) Arrow D
- 21. In this graphic representation of a chemical reaction, which arrow depicts the potential energy of the products?
  - (a) Arrow A
  - (b) Arrow B
  - (c) Arrow C
  - (d) Arrow D

22. In this graphic representation of a chemical reaction, which arrow depicts the heat of the reaction for the forward reaction?

- (a) Arrow A
- (b) Arrow B
- (c) Arrow C
- (d) Arrow D

23. Examine the following diagram and answer the questions.



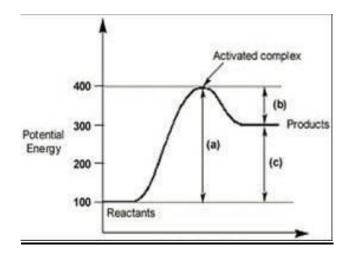
In this graphic representation of a chemical reaction

- (1) arrow A depicts
- (2) arrow B depicts\_\_\_\_\_
- (3) arrow C depicts\_\_\_\_\_
- (4) arrow D depicts\_\_\_\_\_
- (5) arrow X depicts\_\_\_\_\_
  - (a) The potential energy of the reactants
  - (b) The potential energy of the products
  - (c) The heat of the reaction for the forward reaction
  - (d) The activation energy of the forward reaction
  - (e) The activation energy of the reverse reaction

*Draw the missing arrow X at the diagram.* 

Is this reaction exothermic or endothermic?

24. Examine the following diagram and answer the questions

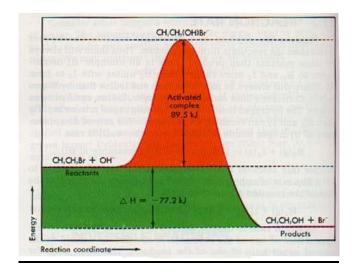


In this graphic representation of a chemical reaction

- (1) arrow (a) depicts\_\_\_\_\_
- (2) arrow (b) depicts
- (3) arrow (c) depicts

Is this reaction *exothermic* or *endothermic*?

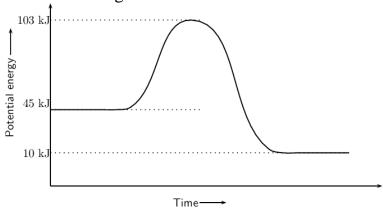
Questions 25-26 refer to the Diagram 2



#### Diagram 2

- 25. Calculate the activation energy value of the reverse reaction, using the Diagram 2 data.
- 26. Determine the enthalpy value of the reverse reaction, using the Diagram 2 data.

Questions 27-33 refer to the Diagram 3



# Diagram 3

- 27. In this graphic representation of a chemical reaction the potential energy of the reactants is
- (a) 10 kJ
- (b) 45 kJ
- (c) 58 kJ
- (d) 93 kJ
- (e) 103 kJ
- 28. In this graphic representation of a chemical reaction the potential energy of the products is
- (a) 10 kJ
- (b) 45 kJ
- (c) 58 kJ
- (d) 93 kJ
- (e) 103 kJ

29. In this graphic representation of a chemical reaction the activation energy of the forward reaction is (a) 10 kJ (b) 45 kJ (c) 58 kJ (d) 93 kJ (e) 103 kJ
30. In this graphic representation of a chemical reaction the activation energy of the reverse reaction is (a) 10 kJ (b) 45 kJ (c) 58 kJ (d) 93 kJ (e) 103 kJ
31. In this graphic representation of a chemical reaction the heat of the reaction of the forward reaction is (a) $+10 \text{ kJ}$ (b) $-35 \text{ kJ}$ (c) $+35 \text{ kJ}$ (d) $-45 \text{ kJ}$ (e) $+45 \text{ kJ}$
32. In this graphic representation of a chemical reaction the heat of the reaction of the reverse reaction is  (a) +10 kJ  (b) -35 kJ  (c) +35 kJ  (d) -45 kJ  (e) +45 kJ
33. In this graphic representation of a chemical reaction indicate the difference between the activation energies for the forward and reverse reactions and equals the energy change in the reaction  (a) +10 kJ  (b) -35 kJ  (c) +35 kJ  (d) -45 kJ  (e) +45 kJ
34. Diluted hydrochloric acid reacts with marble chips (calcium carbonate), giving off carbon dioxide gas. Which solution of acid will have the fastest initial rate of reaction: (a) 50 ml of 0.5 mol L <sup>-1</sup> , (b) 10 ml of 1.0 mol L <sup>-1</sup> or (c) 25 ml of 0.5 mol L <sup>-1</sup> .

Give explanation.

35. The activation energy for the uncatalysed decomposition of ammonia to its elements is +335 kJ/mol. The enthalpy of reaction for this decomposition is +92 kJ/mol. (a) Calculate the activation energy for uncatalysed formation of ammonia from nitrogen and hydrogen. (b) Determine the standard enthalpy value of ammonia formation reaction, using the given data.

# SELF-STUDY TRAINING

# REDOX REACTIONS AND ELECTROLYSIS QUESTIONS

## For the equations 1-10:

- i. Balance a redox reaction using half-equations.
- ii. Identify oxidizer and reducing agent.
- iii. Give the full systematic names of the reactants and products.
- 1.  $PH_3 + HClO_3 \rightarrow HCl + ...$
- 2.  $PH_3 + HMnO_4 \rightarrow MnO_2 + ... + ...$
- 3.  $P_2O_3 + HNO_3 + ... \rightarrow NO + ...$
- 4.  $PH_3 + AgNO_3 + ... \rightarrow Ag + HNO_3 + ...$
- 5.  $KNO_2 + ... + H_2SO_4 \rightarrow I_2 + NO + ... + ...$
- 6.  $P_2O_3 + H_2Cr_2O_7 + ... \rightarrow H_3PO_4 + CrPO_4$
- 7.  $HCOH + KMnO_4 + ... \rightarrow CO_2 + K_2SO_4 + ... + ...$
- 8.  $FeCl_2 + HNO_3$  (conc.)  $\rightarrow Fe(NO_3)_3 + HCl + ... + ...$
- 9.  $K_2MnO_4 + HCl \rightarrow MnCl_2 + Cl_2 + ... + ...$
- 10.  $Zn + KMnO_4 + ... \rightarrow MnSO_4 + K_2SO_4 + ... + ...$

# **Tasks 11-25:**

- i. Write the reactions that occur during electrolysis (at the cathode and inert anode).
- ii. Indicate oxidation and reduction processes.
- iii. Write overall electrolysis reaction.
- 11. Potassium chloride
  - (a) Solution
  - (b) Melt
- 12. Copper (II) oxide
- 13. Solution of copper (II) bromide
- 14. Copper (II) fluoride
  - (a) Solution
  - (b) Melt

- 15. Solution of aluminium nitrate
- 16. Solution of potassium iodide
- 17. Solution of potassium sulfate
- 18. Solution of copper (II) sulfate
- 19. Solution of silver nitrate
- 20. Solution of sodium hydroxide
- 21. Solution of magnesium nitrate
- 22. Magnesium chloride (melt)
- 23. Solution of sodium phosphate
- 24. Solution of sodium perchlorate
- 25. Solution of sulfuric acid

#### **ANSWERS**

# **END-OF-CHAPTER I QUESTIONS**

#### FUNDAMENTALS OF THERMOCHEMISTRY

- 1. (a) I
  - (b) I
  - (c) II
  - (d) I
  - (e) II
- 2. b
- 3. a
- 4. c
- 5. d
- 6. b
- 7. c
- 8. b
- 9. b
- 10.(a)  $\Delta H_r^o$ 
  - (b)  $\Delta H_f^o$  (CO<sub>2</sub>(g)), or  $\Delta H_c^o$ (C(graphite))
  - (c)  $\Delta H_r^c$
  - (d)  $\Delta H_f^o$  (H<sub>2</sub>O (l)), or  $\Delta H_c^o$ (H<sub>2</sub>(g))
- 11.a
- 12.a
- 13. d
- 14. c
- 15. b
- 16. d
- 17. a
- 18. -100.5 kJ/mol
- 19. -851.5 kJ/mol
- 20. -30.6 kJ/mol
- 21. -802.2 kJ/mol
- 22. -162.0 kJ/mol
- 23. 296.5 L
- 24. (i) -2813 kJ/mol
  - (ii) -78.2 kJ/mol
- 25. -278 kJ/mol
- 26.(a) -85 kJ/mol
  - (b) -86 kJ/mol

<u>Explanation:</u> These are virtually the same, as predicted by Hess's Law. The difference is caused by rounding errors in the data.

- 27.(A) 11.2 L
  - (B) 111 kJ

#### **END-OF-CHAPTER II QUESTIONS**

#### **CHEMICAL EQUILIBRIUM**

- 1. c
- 2. b
- 3. a
- 4. b
- 5. d
- 6. d
- 7. (a) moves to left; more ethanoic acid and ethanol formed; reaction moves in direction to oppose the effect of added ethyl ethanoate, so ethyl ethanoate decreases in concentration
  - (b) moves to left; more ethanoic acid and ethanol formed; reaction moves in direction to oppose the removal of ethanol, so more ethanol (and ethanoic acid) formed from ethyl ethanoate and water.
- 8. (a) moves to right; more Ce<sup>3+</sup> and Fe<sup>3+</sup> formed; reaction moves in direction to oppose the effect to added Fe<sup>2+</sup>; so Ce<sup>4+</sup> and Fe<sup>2+</sup> decrease in concentration
  - (b) no effect; the water dilutes all the ions equally, so there is no change in the ratio of reactants to products.
- 9. Equilibrium shifted to the left as fewer gas molecules on left.
- 10. Equilibrium shifted to the left as no gas molecules on left but carbon dioxide on right.
- 11. Equilibrium shifted to the right as greater number of gas molecules on the right.
- 12. Equilibrium shift to the right as endothermic reaction favours the product.
- 13. Endothermic as the forward reaction is favoured by an increase in temperature.
- $14.K_c = [CH_3OH] / ([CO] [H_2]^2)$
- $15.K_c = ([H_2O]^2 [Cl_2]^2 / ([HCl]^4 [O_2])$
- $16.K_c = [NH_3]^2 / ([N_2] [H_2]^3)$
- $17.K_c = [SO_3]^2 / ([O_2] [SO_2]^2)$
- 18.4.03
- 19.32.7
- 20.319.3
- 21.HCOOH<sub>2</sub><sup>+</sup> is the acid; ClO<sub>2</sub><sup>-</sup> is the base
- 22.H<sub>3</sub>O<sup>+</sup> is the acid; HS<sup>-</sup> is the base
- 23.CH<sub>3</sub>NH<sub>2</sub> is the base on the left-hand side, so CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> is the conjugate acid
- 24.H<sub>2</sub>O is the base on the left-hand side, so H<sub>3</sub>O<sup>+</sup> is the conjugate acid
- 25.OH is the base on the left-hand side, so H<sub>2</sub>O is the conjugate acid
- 26.NH<sub>2</sub>CH<sub>2</sub>COOH is the acid on the left-hand side, so NH<sub>2</sub>CH<sub>2</sub>COO<sup>-</sup> is the conjugate base
- 27.H<sub>3</sub>O<sup>+</sup> is the acid on the left-hand side, so H<sub>2</sub>O is the conjugate base
- 28.NH<sub>2</sub>CH<sub>2</sub>COOH is the base on the left-side, so H<sub>3</sub>N<sup>⊕</sup>CH<sub>2</sub>COOH is the conjugate acid

- 29. Hydrogen ions react with magnesium; ethanoic acid has fewer ions in solution, lower concentration of ions in solution than hydrochloric acid, therefore lower rate of reaction.
- 30.a, c
- 31.a
- 32.c
- 33.(a) Ka =  $c \alpha^2/(1-\alpha)$ 
  - (b)  $[H^{+}] = Ka c/c_{salt}$
- 34. 3.0 kPa
- $35.9.1 \times 10^{-3}$
- $36.1.27 \times 10^{-9}$

# **END-OF-CHAPTER III QUESTIONS**

#### FUNDAMENTALS OF CHEMICAL KINETICS

- 1. a
- 2. b
- 3. c
- 4. d
- 5. d
- 6. the rate will be doubled
- 7. the rate will increase in 27 times
- 8. the rate will increase in 27 times
- 9. the rate will increase in 9 times
- 10.the rate will diminish to one-eight of its initial value
- 11.16 times
- 12.12 times
- 13.1.9
- 14.a
- 15.d
- 16.c
- 17.b
- 18.d
- 19.b
- 20.a
- 21.d
- 22.c
- 23.(1) a
  - (2) d
  - (3) c
  - (4) b
  - (5) e

Exothermic

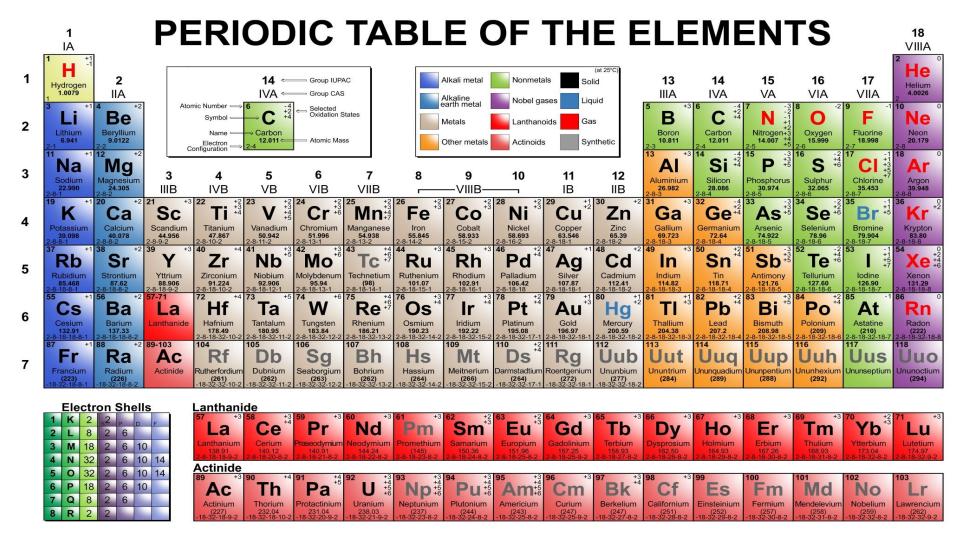
- 24.(1) The activation energy of the forward reaction
  - (2) The activation energy of the reverse reaction
  - (3) The heat of the reaction for the forward reaction Endothermic
- 25.166.7 kJ
- 26.77.2 kJ
- 27.b
- 28.a
- 29.c
- 30.d
- 31.b
- 32.c
- 33.b
- 34.b

<u>Explanation</u>: The more concentrated the acid, the greater the number of hydrogen ions dissolved in given volume of solution, resulting in an increased frequency in collisions between the hydrogen ions and the calcium carbonate. The volume of acid will not affect the initial rate of the reaction.

- 35.(a) 243 kJ/mol
  - (b) -46 kJ/mol

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