

**VIT**Vellore Institute of Technology
(Deemed to be University under section 3 of U.G. Act, 1956)**SCHOOL OF ADVANCED SCIENCES****Department of Chemistry****Fall Semester 2023-24****Continuous Assessment Test – 2****Course Code:** BCHY101L**Duration** : 90 Minutes**Slot** : D2 + TD2**Course Name:** Engineering Chemistry**Max. Marks** : 50**Class Numbers:** VL2023240106213, 6215, 6217, 6219, 6239, 6243, 6247, 6251, 6255, 6264, 6275, 6279, 6283, 6287, 6291**Faculty Names:** Dr. Manish Kumar Mishra, Dr. Sheela A, Dr. Buvanewari G, Dr. Satish Kumar G, Dr. Sriraghavan K, Dr. Karpagam S, Dr. Arunprasad M, Dr. Ravikanth K, Dr. Sai Saraswathi V, Dr. Namrata Deka, Dr. Barnali Maiti, Dr. Chandan Maity, Dr. Madhumitha G. Dr. Buvanewari G. Dr. Veera Venkata Ramesh E

QN	Answer <u>ALL</u> the questions (5 X 10 = 50 Marks)	Marks	CO	BL
1	Derive an expression for the work done by a system (a) having an ideal gas as a working substance wherein heat is absorbed reversibly and without changing the internal energy. (b) having carbon dioxide as a working substance that comes out at high pressure and expands at atmosphere pressure without absorbing heat.	10	CO2	BL3
2	(a) How is Arrhenius equation related to collision theory? Explain how the geometry of an activated complex is different from those of reactant and product with an example. (b) A Carnot engine works between 27 and 127 °C. What is the maximum useful work the engine can do if it is supplied with a 400 kJ of heat energy?	5 + 5	CO2	BL2
3	(a) Distinguish second order and pseudo-first order reactions. How a second order reaction can be converted into a pseudo-first order reaction? Explain with an example. (b) Substance A with an initial concentration of 10 M undergoes decomposition following first order kinetics. After 23 min the concentration of A becomes 1 M. Calculate half-life period of the reaction.	5 + 5	CO2	BL4
4	(a) What are the reaction products formed when salicylic acid reacts with any acetylating agent? Give reaction mechanism. (b) Primary aromatic amine forms a dye through diazotization reaction. Substantiate this statement with appropriate reaction steps.	5 + 5	CO1	BL6

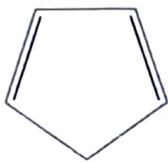
5

How will you convert the following non-aromatic molecules/ion into aromatic molecules/ions? Give suitable explanation along with the aromatic structure in each case.

10

CO1

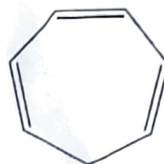
BL5



a) Cyclopentadiene



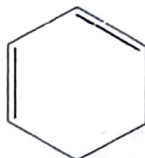
b) Cyclopropene



c) Cycloheptatriene



d) Protonated Pyrrole



e) 1,3 Cyclohexadiene

SCHOOL OF ADVANCED SCIENCES

Department of Chemistry

Fall Semester 2023-24

Continuous Assessment Test – 2

Answer Key

1. Derive an expression for the work done by a system a) having an ideal gas as a working substance wherein heat is absorbed reversibly and without changing the internal energy, b) having carbon dioxide as a working substance that comes out at high pressure and expands at atmosphere pressure without absorbing heat.

Key:

a) (5 M)

➤ Reversible isothermal expansion:

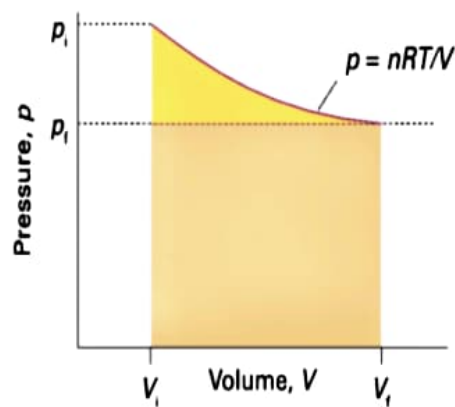
$$w = \int_{v_i}^{v_f} P dv = \int_{v_i}^{v_f} \frac{nRT}{V} dv \quad (\text{as } PV = nRT)$$

(throughout the expansion, $P_{\text{ex}} = P$ as the expansion is reversible)

- Work done by the n moles of gas can be evaluated as:

$$w = -nRT \ln \frac{V_f}{V_i} = -nRT \ln \frac{P_i}{P_f}$$

(since $\frac{V_f}{V_i} = \frac{P_i}{P_f}$ in an isothermal expansion of a perfect gas)



b) (5 M)

➤ Adiabatic process (constant heat)

- no heat is added/ removed from a system.
- 1st law of thermodynamics:

(as no heat is allowed to enter/leave the system, $q = 0$; $\Delta U = w$)

- ✓ Example: A gas expanding so quickly that no heat can be transferred. Due to the expansion work, temperature drops. **This is exactly what happens with a carbon dioxide fire extinguisher, with the gas coming out at high pressure and cooling as it expands at atmos. pressure**

→ **Expansion: $w = -ve$, $\Delta U = -ve$;**

So, **T** of the system falls

⇒ Work is done by the system at the expense of its internal energy

- $w = \Delta U = C_v \Delta T$ (for 1 mole of gas)

- F
- E

2a. How is Arrhenius equation related to collision theory? Explain how the geometry of an activated complex is different from those of reactant and product with an example.

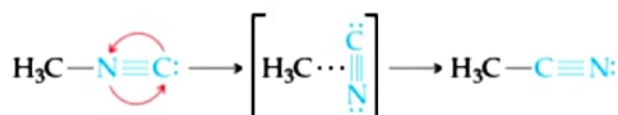
Key:

- According to the kinetic-molecular theory of gases, increasing the temperature increases molecular speeds. As molecules move faster, they collide more forcefully (with more energy) and more frequently, both of which increase the reaction rate.

Arrhenius noted that for most reactions the increase in rate with increasing temperature is nonlinear. The Arrhenius equation gives the dependence of the rate constant of a chemical reaction on the absolute temperature as $k = A e^{-\frac{E_a}{RT}}$.

3 M

The geometry of the activated complex is different from both reactant and product and assumes a transition profile. Example:



Energy profile for conversion of methyl isonitrile (H_3CNC) to its isomer acetonitrile (H_3CCN).

2 M

2b. A Carnot engine works between 27 and 127 °C. What is the maximum useful work the engine can do if it is supplied with a 400 kJ of heat energy?

Key:

$$T_c = 27 + 273 = 300K$$

$$T_h = 127 + 273 = 400K$$

$$q_h = 400 \text{ kJ}$$

$$\text{Maximum useful work, } w = q_h \times \frac{T_h - T_c}{T_h} = 400 \text{ kJ} \times \left(\frac{400 - 300}{400}\right) = 100 \text{ kJ}$$

3a) Distinguish second order and pseudo-first order reactions. How a second order reaction can be converted into a pseudo-first order reaction? Explain with an example.

Key:

Second order reaction	Pseudo-first order reaction
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$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	$\ln[A]_t - \ln[A]_0 = -kt$
$1/[A]_t$ plot is linear	$\ln[A]_t$ plot is linear
$t_{1/2} = \frac{1}{k[A]_0}$	$t_{1/2} = \frac{-\ln \frac{1}{2}}{k} = \frac{0.693}{k}$
Molecularity = 2 Unit of k = L/mol/s	Molecularity = 2 Unit of k = 1/s

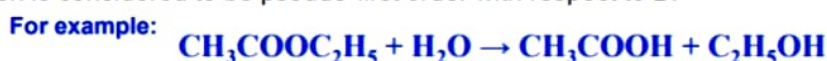
3 M

- This reaction occurs when one reacting material is present in great excess or is maintained at a constant concentration compared with the other substance.



So, if component B is in large excess and the concentration of B is very high as compared to that of A, the reaction is considered to be a **pseudo-first-order reaction** with respect to A.

If component A is in large excess and the concentration of A is very high as compared to that of B, the reaction is considered to be pseudo-first order with respect to B.



2 M

3b. Substance A with an initial concentration of 10 M undergoes decomposition following first order kinetics. After 23 min the concentration becomes 1 M. Calculate half-life period of the reaction.

Key:

$$\ln \frac{[A]_t}{[A]_0} = -kt \quad , \quad \ln \frac{[A]_t}{[A]_0} / t = -k$$

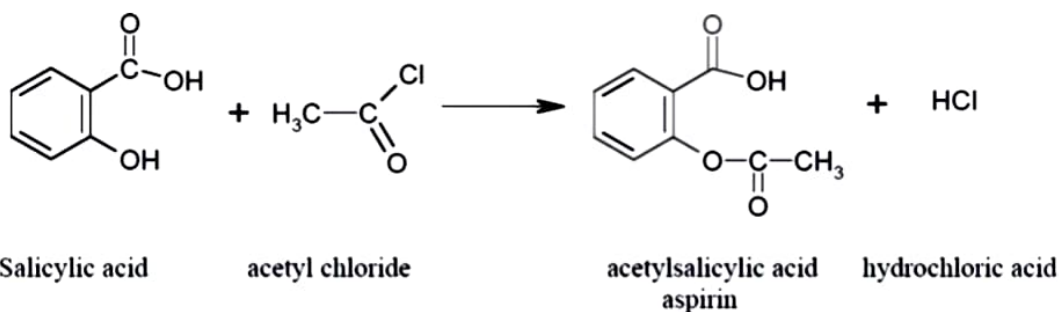
$$k = -\frac{\ln \frac{1}{10}}{23}$$

$$k = 0.1 \text{ min}^{-1}$$

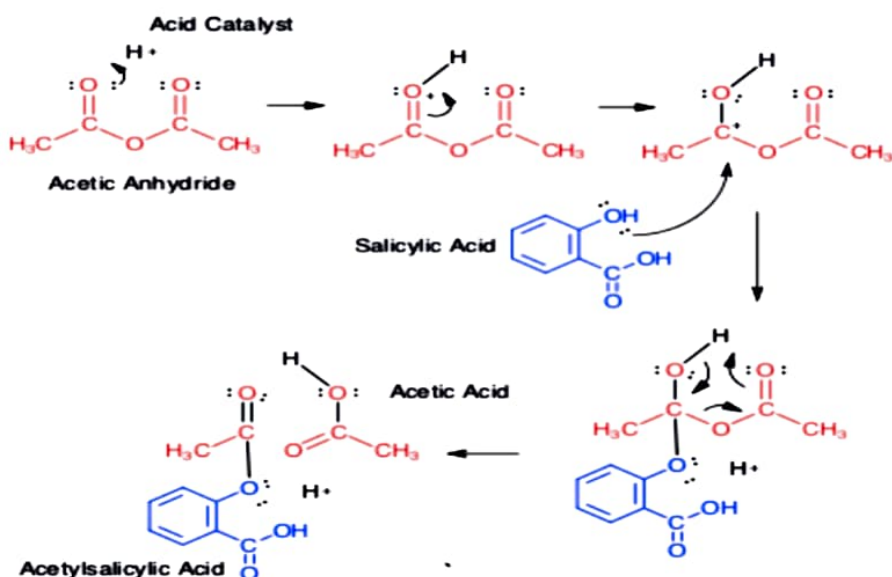
$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{0.1} = 6.93 \text{ min}$$

4a. What are the reaction products formed when salicylic acid reacts with any acetylating agent? Give reaction mechanism.

Key:

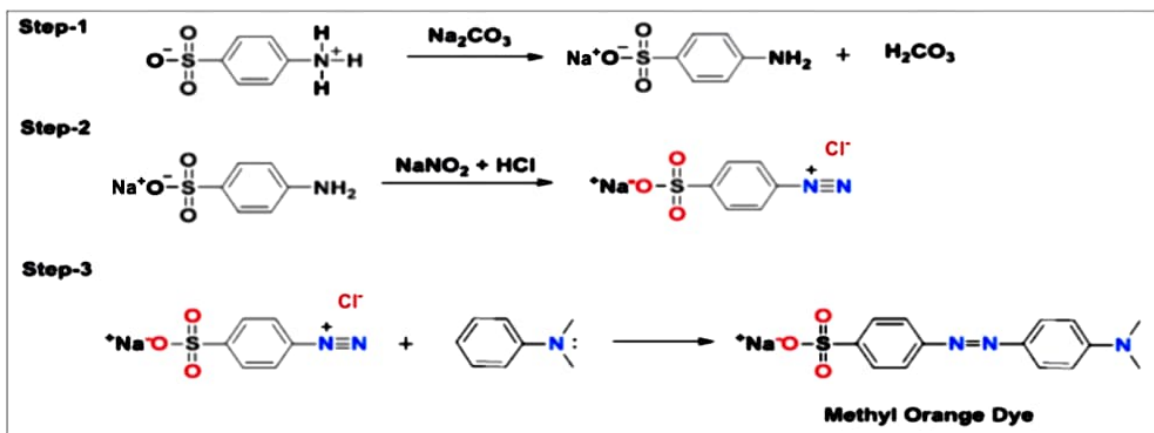


The mechanism will be the same but HCl is formed instead of acetic acid. (5M)



4b. Primary aromatic amine forms a dye through diazotization reaction. Substantiate this statement with appropriate reaction steps.

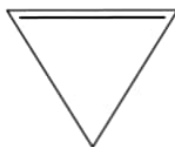
Key: Taking aniline as an example, it can be determined through the dye test as below (5 M)



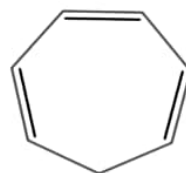
5. How will you convert the following non-aromatic molecules/ions into aromatic molecules/ions? Give suitable explanation along with the aromatic structure in each case.



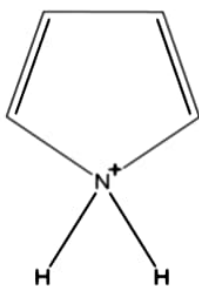
a) Cyclopentadiene



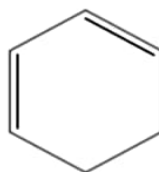
b) Cyclopropene



c) Cycloheptatriene



d) Protonated Pyrrole



e) 1,3 Cyclohexadiene

Key: 2 X 5 = 10M

- Cyclopentadiene – by removing a proton to give cyclopentadienyl anion
- Cyclopropene - by removing H^- to give cyclopropenyl cation
- Cycloheptatriene - by removing H^- to give tropylium ion
- Protonated pyrrole – by removing a proton to give pyrrole
- 1,3 Cyclohexadiene – by removing H_2 to give benzene