

Key to Test 2 for all test versions

Average \pm sdev=87 (58%) \pm 33(22%) Highest: 150Rough Grading Scale for this test: A \geq 120 , B \geq 98 . C \geq 67 D \geq 50

Part I (multiple choice)

1. e	7. b; $v=(-1/b)(\Delta B/\Delta t)=(1/c)(\Delta C/\Delta t)$
2. d	8. d; $v=k[Co]; k = v/[Co] = 3.2 \times 10^{-7} \text{Mmin}^{-1} / 1.14 \times 10^{-3} \text{M} = 2.8 \times 10^{-4} \text{min}^{-1}$
3. e	9. d
4. d	10. a; $\ln C = \ln C_0 - kt \Rightarrow \ln(C/C_0) = -kt \Rightarrow$
5. a	$t = -(1/k)\ln(.75) = -(1/3.33\text{h})(-.288) = 0.086$
6. a	11. a

Part II, Problems

a) Solution: **Second order** kinetics. It is imperative to draw 3 graphs. (i) Graph [A] vs t, (ii) $\ln[A]$ vs t and (iii) $1/[A]$ vs t. You discover that only the plot of **$1/[A]$ vs t** yields a **straight line**. This is the clear proof that it is second order.

b. Solution: Since $1/A = 1/A_0 + kt$, the slope of the line is k. Answers will vary slightly according to the graph but here's an example:

$$\{(1/99.9 - 1/25)\text{mM}^{-1}\} / \{30-0\}\text{min} = \mathbf{1.00 \times 10^{-3} \text{ mM}^{-1} \text{ min}^{-1}}.$$

c. Solution: Since $1/A = 1/A_0 + kt$, $= 1/99.9\text{mM} + (1 \times 10^{-3}/\text{mM min})(50\text{min})$
 $= 6.0 \times 10^{-2} \text{ mM}^{-1} \Rightarrow [A] = (1/6.0 \times 10^{-2} \text{ mM}^{-1}) = \mathbf{16.7 \text{ mM}}$

2. a) Solution: Arrhenius equation: $k = Ae^{-E_a/RT} \Rightarrow \ln k = \ln A - E_a/RT$
 $\Rightarrow \ln(k_2/k_1) = (E_a/R)(1/T_1 - 1/T_2)$; $\ln(2) = (E_a / 8.314 \text{ J/molK})(298^{-1} - 308^{-1})\text{K}^{-1}$
 $\Rightarrow E_a = 52,900 \text{ J/mol} = \mathbf{52.9 \text{ kJ/mol}}$

b) Solution: Start off with the Arrhenius equation again:

$$k = Ae^{-E_a/RT} \Rightarrow \ln k = \ln A - E_a/RT \Rightarrow \ln(k_2/k_1) = -(E'_a - E_a)/RT$$

$$\Rightarrow \text{call: } \Delta E_a = -(E_a - E'_a) = E_a - E'_a$$

$$\Delta E_a = RT \ln(k_2/k_1); \Delta E_a = (8.314)(298) \ln(30000) = 25.5 \text{ kJ/mol} = E_a - E'_a$$

$$\text{But } E_a = 52.9 \text{ kJ/mol (from (a) above). } E'_a = (52.9 - 25.5) = \mathbf{27.4 \text{ kJ}}$$

3. Solution: Start with slowest step, step (2): $v = k_2[\text{Br}][\text{H}_2]$ but Br is an intermediate so, we have to solve for it: At steady state, we have:

$$d[\text{Br}]/dt = k_1[\text{Br}_2] - k_{-1}[\text{Br}]^2 - k_2[\text{Br}][\text{H}_2] = 0 \Rightarrow [\text{Br}]^2 k_{-1} + [\text{Br}][\text{H}_2] k_2 = k_1[\text{Br}_2]$$

\Rightarrow assuming that $k_2 \ll k_{-1}$ such that the previous equation reduces to:

$$[\text{Br}]^2 k_{-1} \approx k_1[\text{Br}_2] \Rightarrow [\text{Br}] = \{k_1/k_{-1}[\text{Br}_2]\}^{1/2}; \text{ and voila!}$$

$$v = k'[\text{Br}_2]^{1/2}[\text{H}_2]$$

It is 3/2 order, 1st order in H_2 and 1/2 order in $[\text{Br}_2]$.

4. Solution: $d = m/V$ where we will use: $m =$ mass of a unit cell, $V =$ volume of a unit cell.

for body centered: $c^2 = (2a^2) + a^2 = (4r)^2$; $3a^2 = 16r^2$; Or $a = \{16r^2/3\}^{1/2} = 4r/\sqrt{3}$;

$V_{\text{uc}} = a^3 = 12.3r^3$. There are 2 atoms per u.cell. so $m = 2(23.0)(1/6.02 \times 10^{23}) = 7.64 \times 10^{-23} \text{g}$

$$V_{\text{uc}} = 12.3 r^3 = m/d = 7.64 \times 10^{-23} \text{g} / 0.968 \text{g./cm}^3$$

$$r^3 = 6.42 \times 10^{-24} \Rightarrow r = 1.86 \times 10^{-8} \text{ cm} = \mathbf{1.86 \text{ \AA}}$$

5. Solution: $\ln(P_2/P_1) = (\Delta H_{\text{vap}}/R)(1/T_1 - 1/T_2)$;

here: $P_2 = 760 \text{ mmHg}$, $P_1 = 23.76 \text{ mmHg}$, $T_1 = 298 \text{ K}$, $T_2 = 373 \text{ K}$

$$\Delta H = R \{ \ln(P_2/P_1) \} / \{ (1/T_1 - 1/T_2) \} = (8.314)(\ln(760/23.76)) / \{ 1/298 - 1/373 \}$$

$$= 4.27 \times 10^4 \text{ J/mol} = \mathbf{42.7 \text{ kJ/mol.}}$$

b) Solution: Here, it is again convenient to use the Clausius-Clapeyron equation:

$$\ln(P_2/P_1) = (\Delta H_{\text{vap}}/R)(1/T_1 - 1/T_2);$$

here: $P_2 = ?$, $P_1 = 23.76 \text{ mmHg}$, $T_1 = 298 \text{ K}$, $T_2 = 310 \text{ K}$

$$\ln(P_2/P_1) = (4.27 \times 10^4 \text{ J/mol} / 8.314 \text{ J/molK}) (1/298 - 1/310) = 0.667 \Rightarrow P_2/23.76$$

$= e^{0.667} = 46.2 \text{ mmHg}$, but this is at 100% humidity.

at 73% humidity, that would be $P_{\text{H}_2\text{O}} = (46.2)(.73) = \mathbf{33.7 \text{ mmHg}}$