

Possible constants/conversions to use:

$$R = 8.31451 \text{ J K}^{-1} \text{ mol}^{-1} = 0.083145 \text{ dm}^3 \text{ bar K}^{-1} \text{ mol}^{-1} = 0.0821 \text{ Lit atm K}^{-1} \text{ mol}^{-1}$$

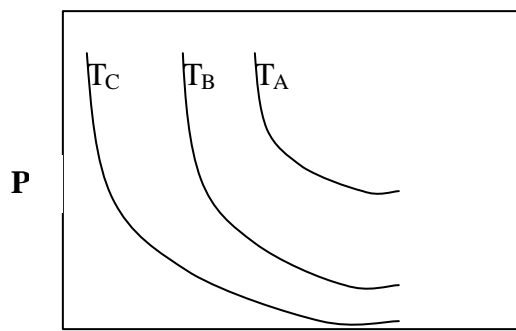
$$\text{Avogadro's } \# = N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$h = \text{planck's constant} = 6.626 \times 10^{-34} \text{ J s}$$

$$10^9 \text{ nm} = 1 \text{ m} \quad 10 \text{ dm} = 1 \text{ m}$$

$$\text{Kelvin} = \text{Celsius} + 273.15$$

1. (3 pts) Assuming the ideal gas model list the isotherms ( $T_A$ ,  $T_B$ , and  $T_C$ ) in the left figure from highest T to lowest T.



\_\_\_\_\_ > \_\_\_\_\_ > \_\_\_\_\_  
(highest T) (lowest T)

2. (3 Pts) If you doubled the pressure and doubled the temperature of an ideal gas what becomes of the volume?

- It increases by a factor of 4.
- It increases by a factor of 2.
- It remains the same.
- It decreases by a factor of 4.

3. (3 Pts) Which of the following is **not** a postulate of Kinetic Molecular Theory?

- Collisions between the particles and the wall are *elastic*.
- The average *translational kinetic energy* of particles is proportional to the absolute temperature
- The *intrinsic volume* of particles is small compared to the volume of the container.
- A gas is composed of a *large number* of particles in constant motion.
- The gas pressure decreases with increasing *intermolecular attractive force*.

4. (3 Pts) Which of the following statements is **false** with regards to proposed mechanisms?

- For an elementary step, the order for each reactant may be explicitly stated.
- If the rate law from the proposed mechanism matches observed data, the proposed mechanism is indeed the actual mechanism.
- The *Steady State* approximation may be utilized for intermediates if the production and depletion rates are approximately equal.
- For a 3-step mechanism in which the reversible steps are fast compared to the last step (slow), the pre-equilibrium approach may be utilized to find the rate law.

5. (3 Pts) Which of the following statements is **false** with regards to the Arrhenius equation which relates the rate constant ( $k$ ) to temperature ( $T$ )?

- The activation energy may be obtained from the slope of a  $\ln k$  vs.  $T$  plot.
- As the temperature increases the rate constant increases.
- A reaction with zero activation energy is largely temperature independent.
- The pre-exponential factor,  $A$ , has the same dimensions as the rate constant,  $k$ .

----- End of qualitative section -----

For the questions below: **SHOW YOUR WORK!!!**

6. (12 Pts) Compute the time between collisions experienced by an  $O_2$  ( $M = 32 \text{ g mol}^{-1}$ ) molecule for a pressure of 0.75 bar at 298.15 K, given  $\sigma = 0.410 \text{ nm}^2$  using the following formula for the collision frequency for a single molecule:  $z = \frac{\sqrt{2} N_A \sigma c P}{RT}$  and  $c = 482 \text{ m s}^{-1}$ .

7. (12 pts) An overall reaction is zeroth order in reactant [A] such that the rate law for [A]  $\rightarrow$  product is given by:

$$\text{rate} = -\frac{d[A]}{dt} = k[A]^0 = k \text{ and the integrated rate law is } [A] - [A]_0 = -kt$$

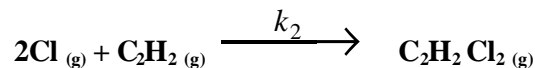
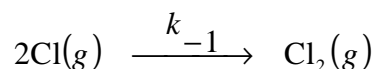
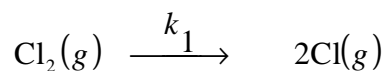
- (3 pts) Given concentration & time data in the form of several ( $[A]_0$ , t) data pair, what quantities would you plot to determine the rate constant, i.e. specify the y-axis quantity and the x-axis quantity.
- (3 pts) If the initial concentration of A is doubled, quantitatively how does the initial rate change?
- (6 pts) Express the half-life  $\tau_{1/2}$  of A in terms of initial concentration  $[A]_0$  and rate constant k.

8. (12 pts) A rate constant of  $5.45 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  is observed at 298.15 K and a rate constant of  $2.47 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  is observed at 596.30 K. Use the Arrhenius expression

$k = A \exp\left(-\frac{E_a}{RT}\right)$  to answer the following questions:

- (4 pts) If you had many values of k at different T instead of just two, which quantities would you plot to determine A and  $E_a$ , i.e. specify the y-axis quantity and the x-axis quantity?
- (8 pts) Determine the value of  $E_a$  in units of  $\text{kJ mol}^{-1}$ .

9. (14 pts) The mechanism for the overall reaction  $C_2H_2(g) + Cl_2(g) \xrightarrow{k} C_2H_2Cl_2(g)$  is given by the following elementary reactions.



- (8 pts) Utilize the steady state approximation (or other methods) to determine the rate law (differential form).
- (2 pts) Simplify the result for the rate law of part a if  $k_2[C_2H_2] \gg k_{-1}$
- (2 pts) Simplify the result for the rate law of part a if  $k_{-1} \gg k_2[C_2H_2]$
- (2 pts) Which result, part b or part c would be consistent with the pre-equilibrium approximation.

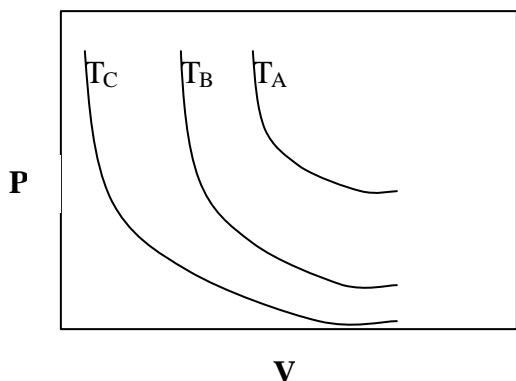
10. (12 pts) For the overall reaction  $A \rightarrow P$  the {time, concentration} data is:

t (seconds)	0	10	20	30	40
[A](mol L <sup>-1</sup> )	$8.57 \times 10^{-4}$	$6.04 \times 10^{-4}$	$4.68 \times 10^{-4}$	$3.84 \times 10^{-4}$	$3.22 \times 10^{-4}$

- (4 pts) If the reaction is second order in A, which quantities would you plot to determine the rate constant, i.e. specify the y-axis quantity and the x-axis quantity?
- (8 pts) Determine the value of the 2<sup>nd</sup> order rate constant with the appropriate units. **SHOW YOUR WORK.** (you may use approximate methods, i.e. you need not use all of the data).

## ANSWERS

1. (3 pts) Assuming the ideal gas model list the isotherms ( $T_A$ ,  $T_B$ , and  $T_C$ ) in the left figure from highest T to lowest T.



$T_A$  (highest T) >  $T_B$  (lowest T) >  $T_C$

2. (3 Pts) If you doubled the pressure and doubled the temperature of an ideal gas what becomes of the volume?

- It increases by a factor of 4.
- It increases by a factor of 2.
- It remains the same.
- It decreases by a factor of 4.

3. (3 Pts) Which of the following is **not** a postulate of Kinetic Molecular Theory?

- Collisions between the particles and the wall are *elastic*.
- The average *translational kinetic energy* of particles is proportional to the absolute temperature
- The *intrinsic volume* of particles is small compared to the volume of the container.
- A gas is composed of a *large number* of particles in constant motion.
- The gas pressure decreases with increasing intermolecular attractive force.

4. (3 Pts) Which of the following statements is **false** with regards to proposed mechanisms?

- For an elementary step, the order for each reactant may be explicitly stated.
- If the rate law from the proposed mechanism matches observed data, the proposed mechanism is indeed the actual mechanism.
- The *Steady State* approximation may be utilized for intermediates if the production and depletion rates are approximately equal.
- For a 3-step mechanism in which the reversible steps are fast compared to the last step (slow), the pre-equilibrium approach may be utilized to find the rate law.

5. (3 Pts) Which of the following statements is **false** with regards to the Arrhenius equation which relates the rate constant ( $k$ ) to temperature ( $T$ )?

- The activation energy may be obtained from the slope of a  $\ln k$  vs.  $T$  plot.
- As the temperature increases the rate constant increases.
- A reaction with zero activation energy is largely temperature independent.
- The pre-exponential factor,  $A$ , has the same dimensions as the rate constant,  $k$ .

6. (12 Pts) Compute the time between collisions experienced by an  $O_2$  ( $M = 32 \text{ g mol}^{-1}$ ) molecule for a pressure of 0.75 bar at 298.15 K, given  $\sigma = 0.410 \text{ nm}^2$  using the following formula for the collision

frequency for a single molecule:  $z = \frac{\sqrt{2} N_A \sigma c P}{RT}$  and  $c = 482 \text{ m s}^{-1}$ .

ANSWER:  $Z^{-1}$  = time between collisions

$$t = \frac{RT}{\sqrt{2} N_A s c P} = \frac{0.083145 \text{ dm}^3 \frac{\text{m}^3}{10^3 \text{ dm}^3} \text{ bar} \times \text{K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}{\sqrt{2} \times 6.02 \times 10^{23} \text{ mol}^{-1} \times 0.410 \text{ nm}^2 \frac{1 \text{ m}^2}{10^{18} \text{ nm}^2} \times 482 \text{ ms}^{-1} \times 0.75 \text{ bar}} = 1.96 \times 10^{-10} \text{ s}$$

7. (12 pts) An overall reaction is zeroth order in reactant [A] such that the rate law for [A] → product is given by:

$$\text{rate} = -\frac{d[A]}{dt} = k[A]^0 = k \text{ and the integrated rate law is } [A] - [A]_0 = -kt$$

a. (3 pts) Given concentration & time data in the form of several ([A]<sub>0</sub>, t) data pair, what quantities would you plot to determine the rate constant, i.e. specify the y-axis quantity and the x-axis quantity.

ANSWER: plot [A] vs. t or [A]-[A]<sub>0</sub> vs. t

b. (3 pts) If the initial concentration of A is doubled, quantitatively how does the initial rate change?

Answer: No effect, the initial rate does not change.

c. (6 pts) Express the half-life  $t_{1/2}$  of A in terms of initial concentration [A]<sub>0</sub> and rate constant k.

$$[A] - [A]_0 = -kt \Rightarrow \frac{[A]_0}{2} - [A]_0 = -k t_{1/2} \Rightarrow t_{1/2} = \frac{[A]_0}{2k}$$

8. (12 pts) A rate constant of  $5.45 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  is observed at 298.15 K and a rate constant of  $2.47 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  is observed at 596.30 K. Use the Arrhenius expression

$k = A \exp\left(-\frac{E_a}{RT}\right)$  to answer the following questions:

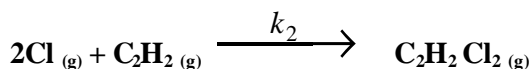
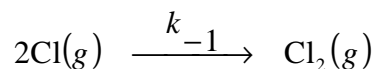
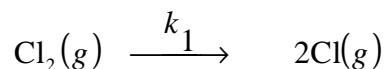
a. (4 pts) If you had many values of k at different T instead of just two, which quantities would you plot to determine A and E<sub>a</sub>, i.e. specify the y-axis quantity and the x-axis quantity?

Answer:  $\ln k = \ln A - E_a/RT$  thus plot  $\ln k$  (y-axis) vs  $1/T$  (x-axis)

b. (8 pts) Determine the value of E<sub>a</sub> in units of kJ mol<sup>-1</sup>.

$$\begin{aligned} \ln k_1 = \ln A - \frac{E_a}{RT_1} &\Rightarrow \ln k_2 = \ln A - \frac{E_a}{RT_2} \Rightarrow \ln k_2 - \ln k_1 = -\frac{E_a}{RT_2} - \left(-\frac{E_a}{RT_1}\right) \\ \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) &\Rightarrow E_a = R \left(\frac{1}{T_1} - \frac{1}{T_2}\right)^{-1} \ln \frac{k_2}{k_1} \\ = 8.3145 \text{ JK}^{-1} \text{ mol}^{-1} \left(\frac{1}{298.15 \text{ K}} - \frac{1}{596.30 \text{ K}}\right)^{-1} \ln \frac{2.47 \times 10^{-4}}{5.45 \times 10^{-5}} &= 7.492 \times 10^3 \text{ J mol}^{-1} = 7.492 \text{ kJ mol}^{-1} \end{aligned}$$

9. (14 pts) The mechanism for the overall reaction  $\text{C}_2\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \xrightarrow{k} \text{C}_2\text{H}_2\text{Cl}_2(\text{g})$  is given by the following elementary reactions.



a. (8 pts) Utilize the steady state approximation (or other methods) to determine the rate law (differential form).

$$\frac{1}{2} \frac{d[Cl]}{dt} = k_1 [Cl_2] \quad \text{and} \quad -\frac{1}{2} \frac{d[Cl]}{dt} = k_{-1} [Cl]^2 \quad \text{and} \quad -\frac{1}{2} \frac{d[Cl]}{dt} = k_2 [Cl]^2 [C_2H_2]$$

$$\frac{d[Cl]}{dt} = 2k_1 [Cl_2] - 2k_{-1} [Cl]^2 - 2k_2 [Cl]^2 [C_2H_2] = 0 \Rightarrow [Cl]^2 = \frac{k_1 [Cl_2]}{k_{-1} + k_2 [C_2H_2]}$$

$$\frac{d[C_2H_2Cl_2]}{dt} = k_2 [C_2H_2] [Cl]^2 = \frac{k_2 k_1}{k_{-1} + k_2 [C_2H_2]} [Cl_2] [C_2H_2]$$

- b. (2 pts) Simplify the result for the rate law of part a if  $k_2 [C_2H_2] \gg k_{-1}$

$$\frac{d[C_2H_2Cl_2]}{dt} = \frac{k_2 k_1}{0 + k_2 [C_2H_2]} [Cl_2] [C_2H_2] = k_1 [Cl_2]$$

- c. (2 pts) Simplify the result for the rate law of part a if  $k_{-1} \gg k_2 [C_2H_2]$

$$\frac{d[C_2H_2Cl_2]}{dt} = \frac{k_2 k_1}{k_{-1} + 0} [Cl_2] [C_2H_2] = \frac{k_2 k_1}{k_{-1}} [Cl_2] [C_2H_2]$$

- d. (2 pts) Which result, part b or part c would be consistent with the pre-equilibrium approximation.

**Answer: part d, since this would have the slow step as last step and the reversible steps as fast.**

10. (12 pts) For the overall reaction  $A \rightarrow P$  the {time, concentration} data is:

t (seconds)	0	10	20	30	40
[A](mol L <sup>-1</sup> )	$8.57 \times 10^{-4}$	$6.04 \times 10^{-4}$	$4.68 \times 10^{-4}$	$3.84 \times 10^{-4}$	$3.22 \times 10^{-4}$

- a. (4 pts) If the reaction is second order in A, which quantities would you plot to determine the rate constant, i.e. specify the y-axis quantity and the x-axis quantity?

**Answer: plot  $1/[A]$  vs  $t$**

- b. (8 pts) Determine the value of the 2<sup>nd</sup> order rate constant with the appropriate units. **SHOW YOUR WORK.** (you may use approximate methods, i.e. you need not use all of the data).

**Answer: Let's take the first and last point:**

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt \Rightarrow k = \frac{\frac{1}{[A]} - \frac{1}{[A]_0}}{t} = \frac{\frac{1}{3.22 \times 10^{-4} \text{ mol L}^{-1}} - \frac{1}{8.57 \times 10^{-4} \text{ mol L}^{-1}}}{40 \text{ s}} = 48.5 \text{ L mol}^{-1} \text{ s}^{-1}$$