

1. A reaction has a rate constant of $2.68 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$. The reaction starts with a reactant concentration of 0.150 M .

a. Calculate the **half-life of the reaction in seconds**.

The reaction is second order as indicated by the units on the rate constant.

$$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{(2.68 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1})(0.150 \text{ M})} = 2.49 \times 10^5 \text{ s}$$

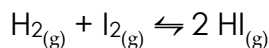
b. Calculate the **number of minutes** required for the concentration to drop to 40.0% of its initial value.

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$
$$t = \frac{\frac{1}{[A]_t} - \frac{1}{[A]_0}}{k} = \frac{\frac{1}{(0.400)(0.150 \text{ M})} - \frac{1}{(0.150 \text{ M})}}{2.68 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}} \times \frac{1 \text{ min}}{60 \text{ s}} = 6.22 \times 10^3 \text{ min}$$

c. Calculate the **molar concentration of the reactant** after 10.0 hours have elapsed.

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} = (2.68 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1})(10.0 \text{ h}) \left(\frac{60 \text{ min}}{1 \text{ h}} \right) \left(\frac{60 \text{ s}}{1 \text{ min}} \right) + \frac{1}{0.150 \text{ M}} = 7.653146667 \text{ M}^{-1}$$
$$[A]_t = 0.131036411 \text{ M} = 0.131 \text{ M}$$

2. The following reaction is allowed to come to equilibrium at 400.0 K in a 5.00 L container



The equilibrium constant, K_p , for this reaction is 33.8 at the given temperature. If the reaction is started with $[\text{H}_2] = 0.25 \text{ M}$, $[\text{I}_2] = 0.50 \text{ M}$ and $[\text{HI}] = 2.50 \text{ M}$, what are the **equilibrium partial pressures** of all substances?

Because $\Delta n = 0$, the values for K_p and K_c are the same.

$$Q_c = Q_p = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2.50)^2}{(0.25)(0.50)} = 50. > 33.8 = K$$

This indicates that the reaction must shift to the left.

	H_2	I_2	HI
Initial	0.25	0.50	2.50
Change	+x	+x	-2x
Equilibrium	0.25+x	0.50+x	2.50-2x

$$K_p = K_c = 33.8 = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2.50 - 2x)^2}{(0.25 + x)(0.50 + x)} = \frac{4x^2 - 10x + 6.25}{x^2 + 0.75x + 0.125}$$

$$33.8x^2 + 25.35x + 4.225 = 4x^2 - 10x + 6.25$$

$$29.8x^2 + 35.35x - 2.025 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = -1.240998, 0.0547567$$

We choose the positive value here which gives equilibrium **concentrations** of $[\text{H}_2] = 0.30 \text{ M}$, $[\text{I}_2] = 0.55 \text{ M}$ and $[\text{HI}] = 2.40 \text{ M}$.

$$P_{\text{H}_2} = MRT = (0.30 \text{ M})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(400.0 \text{ K}) = 9.8 \text{ atm}$$

$$P_{\text{I}_2} = MRT = (0.55 \text{ M})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(400.0 \text{ K}) = 18. \text{ atm}$$

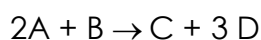
$$P_{\text{HI}} = MRT = (2.40 \text{ M})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(400.0 \text{ K}) = 78.8 \text{ atm}$$

Check :

$$\frac{(78.8)^2}{(9.8)(18)} = 35.2$$

This is close to the value for K_p when we take into account rounding differences.

3. The following kinetic data were taken for the reaction



At 25.0°C			
Exp.	[A] ₀ (M)	[B] ₀ (M)	Rate ₀ (M s ⁻¹)
1	0.1500	0.0368	2.568×10 ⁻⁴
2	0.3000	0.0368	2.054×10 ⁻³
3	0.1500	0.0736	5.136×10 ⁻⁴
At 37.0°C			
4	0.1500	0.0368	6.089×10 ⁻⁴

a. Determine the **rate law** for this reaction. Include in your rate law the rate constant at 25.0°C with units.

The rate increases by a factor of 8 when [A] doubles so the reaction is third order with respect to A ($2^3=8$).

The rate increases by a factor of 2 when [B] doubles so the reaction is first order with respect to B. ($2^1=2$)

The rate law is $\text{rate}=k[A]^3[B]$. The rate constant is:

$$k = \frac{\text{Rate}}{[A]^3 [B]} = \frac{2.568 \times 10^{-4} \text{ M s}^{-1}}{(0.1500 \text{ M})^3 (0.0368 \text{ M})} = 2.07 \text{ M}^{-3} \text{ s}^{-1}$$

The complete rate law is $\text{rate}=2.07 \text{ M}^{-3} \text{ s}^{-1} [A]^3[B]$.

b. What is the **activation energy** of this reaction in **kJ mol⁻¹**?

$$k^{37.0^\circ\text{C}} = \frac{6.089 \times 10^{-4} \text{ M s}^{-1}}{(0.1500 \text{ M})^3 (0.0368 \text{ M})} = 4.90 \text{ M}^{-3} \text{ s}^{-1}$$

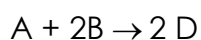
$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$E_a = \frac{R \ln \frac{k_2}{k_1}}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} = \frac{(8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}) \ln \left(\frac{2.07}{4.90} \right)}{\left(\frac{1}{310.2 \text{ K}} - \frac{1}{298.2 \text{ K}} \right)} = 55.2 \text{ kJ mol}^{-1}$$

c. What is the **overall order** of the reaction?

The overall order of the reaction is 4.

4. Determine the **rate law** for the reaction



with the following mechanism.



From the slow step:

$$\text{rate} = k_2 [B][C]$$

From the fast equilibrium:

$$k_1 [A]^2 = k_{-1} [C]$$

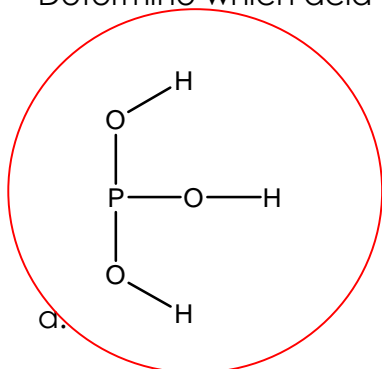
$$[C] = \frac{k_1}{k_{-1}} [A]^2$$

$$\text{Rate} = k_2 \frac{k_1}{k_{-1}} [A]^2 [B]$$

Are there any **intermediates**? **yes** If so, list them **C & E**

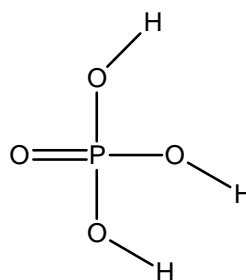
Are there any **catalysts**? **no** If so, list them _____

5. Determine which acid is **weaker**. Circle your answer.



a.

or

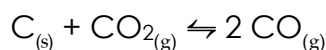


b. HBr

or



7. At 850°C and 1.000 atm pressure, a gaseous mixture of carbon monoxide and carbon dioxide in equilibrium with solid carbon is 90.55% CO by mass.



Calculate K_c for this reaction at 850°C.

If the reaction is at equilibrium and there is 90.55% CO by mass it doesn't matter how much is actually there. We can assume any total mass we want. For simplicity, let's assume there are 100.00 g of gas in the container. Then there are 90.55 g of CO and 9.45 g CO₂. From this we can calculate the needed information. In order to calculate K_c we need to find the concentrations of both gases. For that we need to know how many moles there are of each. We can find moles from mass:

$$90.55 \text{ g CO} \times \frac{1 \text{ mol CO}}{28.0101 \text{ g CO}} = 3.23276 \text{ mol CO}$$

$$9.45 \text{ g CO} \times \frac{1 \text{ mol CO}_2}{44.0095 \text{ g CO}_2} = 0.214726 \text{ mol CO}_2$$

Moles, pressure and temperature gives us the volume of the container:

$$V = \frac{n_r RT}{P_r} = \frac{(3.233 \text{ mol} + 0.215 \text{ mol})(0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1})(1123.2 \text{ K})}{1.000 \text{ atm}} = 317.8 \text{ L}$$

Moles and volume gives us concentration:

$$[\text{CO}] = \frac{3.233 \text{ mol CO}}{317.8 \text{ L}} = 0.01017 \text{ M}$$

$$[\text{CO}_2] = \frac{0.215 \text{ mol CO}_2}{317.8 \text{ L}} = 0.0006765 \text{ M}$$

The concentrations give us K_c : $K_c = \frac{[\text{CO}]^2}{[\text{CO}_2]} = \frac{(0.01017)^2}{0.000677} = 0.153$