

Spontaneity and Kinetics



a) 4 pts

$$[\text{F}_2] = 4 \quad \text{rate} = 4 \quad \bullet \text{ 1st order}$$

$$[\text{ClO}_2] = 2 \quad [\text{F}_2] = \frac{1}{2} \quad \bullet \text{ rate stays the same 1st order}$$

$$\text{rate} = k [\text{ClO}_2] [\text{F}_2]$$

b) 2 pts

$$\text{rate} = k [\text{ClO}_2] [\text{F}_2]$$

$$k = \frac{\text{rate}}{[\text{ClO}_2] [\text{F}_2]}$$
$$= \frac{2.4 \times 10^{-3} \frac{\text{mole}}{\text{L}\cdot\text{s}}}{\left(0.010 \frac{\text{mole}}{\text{L}}\right) \left(0.10 \frac{\text{mole}}{\text{L}}\right)}$$

$$= 2.4 \frac{\text{L}}{\text{mol}\cdot\text{s}}$$

c) 1 pt



$$\frac{-\Delta[\text{F}_2]}{\Delta t} = \frac{1/2 \Delta[\text{ClO}_2\text{F}]}{\Delta t}$$

$$= \frac{1}{2} (9.6 \times 10^{-3})$$

$$= 4.8 \times 10^{-3} \frac{\text{mole}}{\text{L}\cdot\text{s}}$$

d) 2 pts

mechanism #1

defense:

- slow step is first order
- three equations add to proper stoichiometry



a) 3 pts

$$[Y] = 2 \quad \text{rate} = 2 \quad \bullet \text{ 1st order } Y$$

$$[X] = 2 \quad [Y] = 2 \quad \bullet \text{ rate} = 2 \\ \text{zero order } X$$

$$\text{rate} = k[Y]$$

b) 2 pts

$$\text{rate} = k[Y]$$

$$k = \frac{\text{rate}}{[Y]} = \frac{7.0 \times 10^{-4} \frac{\text{mole}}{\text{L} \cdot \text{s}}}{0.10 \frac{\text{mole}}{\text{L}}}$$

$$k = 7.0 \times 10^{-3} \frac{1}{\text{s}}$$

c) 2 pts

$$2.3 \log \frac{C_0}{C} = kt$$

$$2.3 \log \frac{0.60}{0.40} = (7.0 \times 10^{-3}) t$$

$$t = 58 \text{ s}$$

d) 2 pts

mechanism 3

defence:

- the rate expression shows that the slow reaction involves only one Y
- mechanism 1 and 2 show that the rate involves both X and Y

29.



$$25^\circ\text{C}$$

$$K_p = 0.281 \text{ atm}$$

a) 2 p + s

$$\begin{aligned}\Delta G^\circ &= -RT \ln K \\ &= -\left(8.31 \frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(298\text{K})(\ln 0.281) \\ &= 3.14 \times 10^3 \frac{\text{J}}{\text{mol}}\end{aligned}$$

b) 4 p + s

$$\Delta H^\circ = \left(193 \frac{\text{J}}{\text{g}}\right)\left(160 \frac{\text{g}}{\text{mol}}\right) = 3.08 \times 10^4 \frac{\text{J}}{\text{mol}}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$

$$= \frac{(3.08 \times 10^4) - (3.14 \times 10^3)}{298}$$

$$= \frac{2.770 \times 10^4 \frac{\text{J}}{\text{mol}}}{298\text{K}} = 92.9 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

c) 2 p + s

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{3.08 \times 10^4}{92.9} = 332 \text{ K}$$

d) 1 p + s

$$\text{vapor pressure} = 0.281$$

$$K_p = P_{\text{Br}_2}$$



$$\Delta H^\circ = -137 \text{ kJ}$$

A) 2 pts

↑ pressure ↑ effective [] ↑ collisions

B) 2 pts

- slight increase in collision frequency
- more molecules have enough energy that many more collisions have the necessary activation energy
- raises reaction rate a great deal

C) 2 pts

- catalytic Ni lowers E_a
- more molecules have needed energy for a reaction

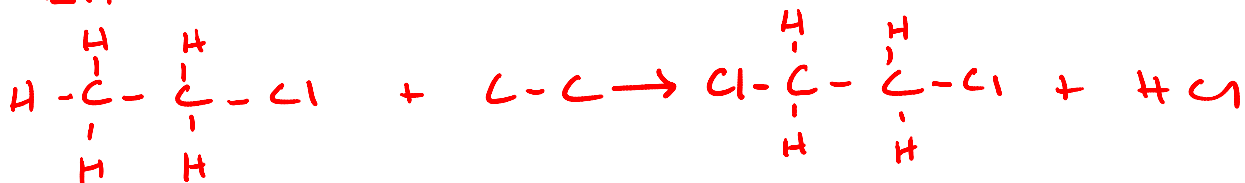
D) 2 pts

- ↑ surface area with powdered Ni
- more catalytic sites means greater rate



a) 2 pts

$\Delta H = \text{bonds broken} - \text{bonds formed}$



$$\Delta H = (2794 + 243) - (2757 + 431)$$

$$\Delta H = 3037 - 3188 = -151 \frac{\text{kJ}}{\text{mol}}$$

b) 4 pts

$$\Delta G = (\Delta G_{\text{FC}_2\text{H}_4\text{Cl}_2}^{\circ} + \Delta G_{\text{FHC}_1}^{\circ}) - (\Delta G_{\text{FC}_2\text{H}_5\text{Cl}}^{\circ} + \Delta G_{\text{FC}_12}^{\circ})$$

$$= (-80.3 + 95.3) - (-60.5 + 0)$$

$$= -115 \text{ kJ}$$

$$\Delta G = \Delta H - T \Delta S$$

$$\Delta S = \frac{[(-151 \text{ kJ}) - (-115 \text{ kJ})]}{298 \text{ K}} = -0.120 \frac{\text{kJ}}{\text{mol} \cdot \text{K}}$$

c. 3 pts

$$\Delta G = -RT \ln K$$

$$-\ln K = \frac{-115000}{(8.314)(298)}$$

$$\ln K = 46.46$$

$$K = 1.50 \times 10^{20}$$

d) 1 pt

- K_{eq} will decrease with an increase in T because the reverse reaction is favored with addition of heat

or

- ΔG will be less negative with an increase in T (From $\Delta G = \Delta H - T\Delta S$) which will cause K to decrease