ANSWER KEY P.S. # 24

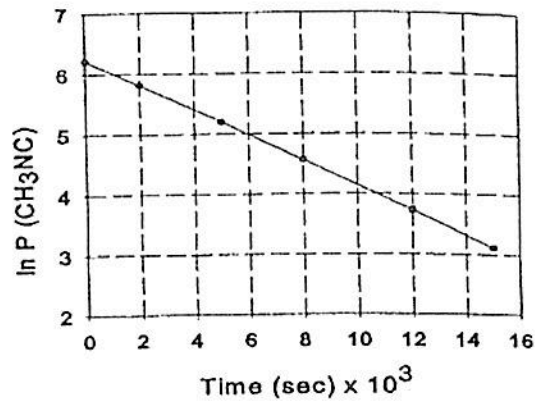
14.30 (a) $t_{1/2} = 0.693/k = 0.693/7.0 \times 10^{-4}\ s^{-1} = 990 = 9.9 \times 10^2\ s$

(b) $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{56.3\ min} \times \frac{1\ min}{60\ s} = 2.052 \times 10^{-4} = 2.05 \times 10^{-4}\ s^{-1}$

14.34

t(s)	P_{CH_3NC}	$\ln P_{CH_3NC}$
0	502	6.219
2000	335	5.814
5000	180	5.193
8000	95.5	4.559
12000	41.7	3.731
15000	22.4	3.109

A graph of ln P vs t is linear with a slope of $-2.08 \times 10^{-4}\ s^{-1}$. The rate constant k = -slope = $2.08 \times 10^{-4}\ s^{-1}$. Half-life = $t_{1/2} = 0.693/k = 3.33 \times 10^3$ s.



14.47 *Analyze/Plan.* Given k_1, at T_1, calculate k_2 at T_2. Change T to Kelvins, then use the Ahrrenius equation [14.21] to calculate k_2. *Solve*:

$T_1 = 20°C + 273 = 293$ K; $T_2 = 60°C + 273 = 333$ K; $k_1 = 2.75 \times 10^{-2} s^{-1}$

(a) $\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{1}{333} - \frac{1}{293}\right) = \frac{75.5 \times 10^3\ J/mol}{8.314\ J/mol}(-4.100 \times 10^{-4})$

$\ln(k_1/k_2) = -3.7229 = -3.72$; $k_1/k_2 = 0.0242 = 0.024$; $k_2 = \frac{0.0275\ s^{-1}}{0.0242} = 1.1\ s^{-1}$

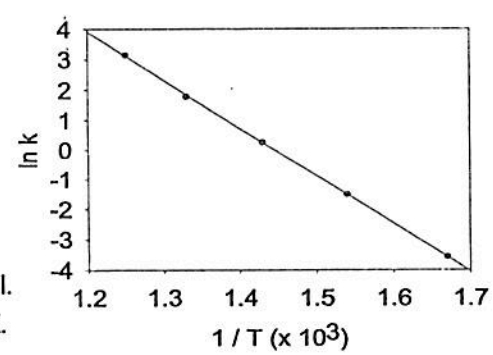
(b) $\ln\left(\frac{k_1}{k_2}\right) = \frac{105 \times 10^3\ J/mol}{8.314\ J/mol}\left(\frac{1}{333} - \frac{1}{293}\right) = -5.1776 = -5.18$

$k_1/k_2 = 5.642 \times 10^{-3} = 5.6 \times 10^{-3}$; $k_2 = \frac{0.0275\ s^{-1}}{5.642 \times 10^{-3}} = 4.9\ s^{-1}$

14.50

k	ln k	T(K)	1/T(× 10^3)
0.028	-3.58	600	1.67
0.22	-1.51	650	1.54
1.3	0.26	700	1.43
6.0	1.79	750	1.33
23	3.14	800	1.25

Using the relationship $\ln k = \ln A - E_a/RT$, the slope, $-15.94 \times 10^3 = -16 \times 10^3$, is $-E_a/R$. $E_a = 15.94 \times 10^3 \times 8.314\ J/mol = 1.3 \times 10^2\ kJ/mol$. To calculate A, we will use the rate data at 700 K. From the equation given above, 0.262 = $\ln A - 15.94 \times 10^3/700$; $\ln A = 0.262 + 22.771$. $A = 1.0 \times 10^{10}$.



14.61 *Analyze/Plan.* Given a proposed mechanism and an observed rate law, determine which step is rate determining. *Solve*:

(a) If the first step is slow, the observed rate law is the rate law for this step.
rate = $k[NO][Cl_2]$

(b) Since the observed rate law is second-order in [NO], the second step must be slow relative to the first step; the second step is rate determining.

14.73 *Analyze/Plan.* Let k = the rate constant for the uncatalyzed reaction,
k_c = the rate constant for the catalyzed reaction

According to Equation [14.22], $\ln k = -E_a/RT + \ln A$

Subtracting ln k from ln k_c,

$$\ln k_c - \ln k = -\left[\frac{55\text{ kJ/mol}}{RT} + \ln A\right] - \left[-\frac{95\text{ kJ/mol}}{RT} + \ln A\right].$$ *Solve*:

(a) RT = 8.314 J/K•mol × 298 K × 1 kJ/1000 J = 2.478 kJ/mol; ln A is the same for both reactions.

$$\ln (k_c/k) = \frac{95\text{ kJ/mol} - 55\text{ kJ/mol}}{2.478\text{ kJ/mol}};\ k_c/k = 1.0 \times 10^7$$

The catalyzed reaction is approximately 10,000,000 (ten million) times faster at 25°C.

(b) RT = 8.314 J/K•mol × 398 K × 1 kJ/1000 J = 3.309 kJ/mol

$$\ln (k_c/k) = \frac{40\text{ kJ/mol}}{3.309\text{ kJ/mol}};\ k_c/k = 1.8 \times 10^5$$

The catalyzed reaction is 180,000 times faster at 125°C.

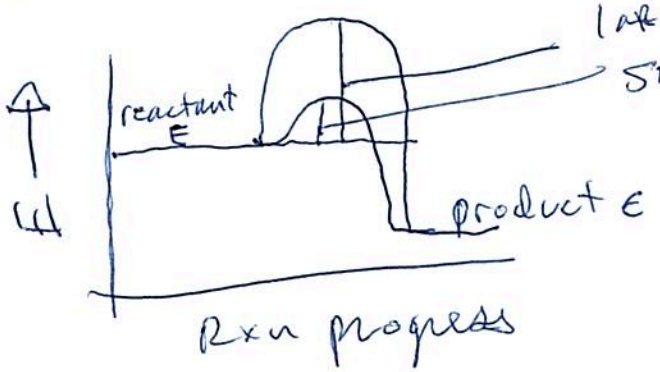
$$H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$$

$$\text{rate} = k[H_2][I_2]$$

(A) If you were to add more $H_{2(g)}$ at a constant T & V, the pressure in the container would ↑, b/c added particles would add more collisions. More collisions = higher rate

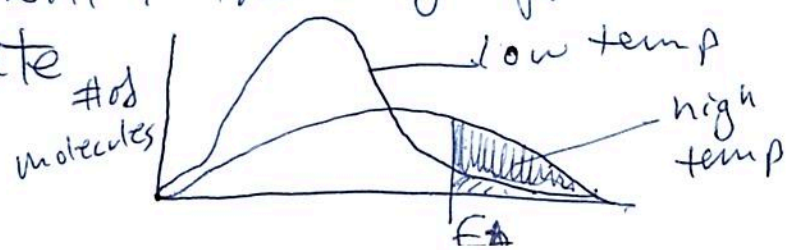
(B) If you were to ↑ Volume, while maintaining temp, the particles would spread out more and the pressure would go down = less collisions = slower (lower) rate.

(C) If you added a catalyst, more reactants would have favorable Rxn energy (be able to overcome activation energy (E_a)). There would be more products forming = ↑ rate



(D) If you ↑ temp, you ↑ the # of particles w/ enough KE to overcome the E_a. This will ↑ the # of effective product forming Rxns = ↑ Rate

Higher temp = larger # of particles in the dark region



$\boxed{\frac{1}{2} \text{ Sheet Key}}$ P.5 #24.

(A(a)) Units for K are zero order Mol/L·sec = M/sec

$[A] = -kt + [A]_0$ $\quad -k = \frac{[A] - [A]_0}{t}$ $\quad \frac{\text{molarity}}{\text{time}}$

(B) Plotting $\frac{1}{[A]}$ vs time yields a straight line w/ positive slope only if the reaction is 2nd order $\frac{1}{[A]} = kt + \frac{1}{[A]_0}$

$y = mx + b$

(C) $\boxed{\text{2nd ORDER}}$ $\quad t_{\frac{1}{2}} = \frac{1}{k[A]_0}$ $\quad$ As $[A]_0 \uparrow$, $t_{\frac{1}{2}} \downarrow$

(D) [A] decreases w/ time in a pattern represented by the graph in $\boxed{\text{1st ORDER}}$ Rxns. If this was zero order, the graph would be a straight line with (−) slope. If 2nd order, $\ln[A] = -kt + \ln[A]_0$ $\propto$ [A] would not look like the graph.

(E) $\boxed{\text{ZERO ORDER}}$ $\quad \text{rate} = k[A]^0 = \boxed{\text{rate} = k}$

if k is constant, so is rate