

Solutions to Equilibrium Practice Problems

Problem 1. Solution:

The expression for $K = \frac{[P_4O_{10}]_{eq}}{[P_4]_{eq}[O_2]_{eq}^5} = 3$

In (a) $Q = \frac{[P_4O_{10}]_{init}}{[P_4]_{init}[O_2]_{init}^5} = \frac{1 M}{1 M \cdot (1 M)^5} = 1 < 3$, the reaction proceeds to the right.

In (b) $Q = \frac{[P_4O_{10}]_{init}}{[P_4]_{init}[O_2]_{init}^5} = \frac{5.0 M}{8.0 M \cdot (0.70 M)^5} = 3.7 > 3$, the reaction proceeds to the left.

Problem 2. Solution:

To determine the final concentrations, the first thing needed are the initial reactant concentrations and an expression for the reaction coefficient Q.

$$[A_{2(g)}] = \frac{1.00 \text{ mol}}{0.250 \text{ L}} = 4.00 \text{ M}, \quad [AB_{(g)}] = [B_{2(g)}] = \frac{2.00 \text{ mol}}{0.250 \text{ L}} = 8.00 \text{ M},$$

$$\text{and } Q = \frac{[AB]_{init}^2}{[A_2]_{init} [B_2]_{init}} = \frac{(8.00)^2}{(4.00)(8.00)} = 2.0$$

The direction of the reaction needs to be determined. To do this, we compare Q vs K.

Since $Q = 2.0 > K = 0.5$, the reaction proceeds to the left.

To determine what final concentrations will be from initial concentrations, a handy tool – the Initial, Change, Equilibrium (ICE) table can be used.

All compounds involved in the reaction are included in an ICE table as follows, with the species that will be consumed on the left side, and the species that will be produced on the right side. Since the reaction proceeds to the left, A₂ and B₂ will be formed and AB will be consumed.

Concentration (M)	2 AB _(g)	A _{2(g)}	B _{2(g)}
Initial	8.00 M	4.00 M	8.00 M
Change	-2x	+x	+x
Equilibrium	8.00 - 2x	4.00 + x	8.00 + x

As the reaction proceeds, x moles of A_{2(g)} and B_{2(g)} are formed as 2x moles of AB_(g) are consumed. Make sure to consider stoichiometric coefficients appropriately.

The equilibrium values are simply the sum of the initial + change concentrations.

Substitute the equilibrium concentrations into K, and solve for x (remember that K is defined for the reaction in the way that it was initially described):

$$K = \frac{[AB]_{eq}^2}{[A_2]_{eq} [B_2]_{eq}} = \frac{(8.00 - 2x)^2}{(4.00 + x)(8.00 + x)} = 0.5$$

so,

$$(8.00 - 2x)^2 = 0.5(4.00 + x)(8.00 + x)$$

$$64 - 32x + 4x^2 = 0.5(32 + 12x + x^2)$$

$$64 - 32x + 4x^2 = 16 + 6x + 0.5x^2$$

$$3.5x^2 - 38x + 48 = 0$$

To solve for x , the quadratic formula must be used,

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{38 \pm \sqrt{(-38)^2 - 4(3.5)(48)}}{2(3.5)} = 1.46 \text{ or } 9.39,$$

Since $2 \times 9.39 = 18.78 > 8.00$ (which would leave the equilibrium concentration of AB at equilibrium negative), then the $x = 1.46$

So, final concentrations are:

$$[A_2] = 4.00 + 1.46 = 5.46 \text{ M}$$

$$[B_2] = 8.00 + 1.46 = 9.46 \text{ M}$$

$$[AB] = 8.00 - 2(1.46) = 5.08 \text{ M}$$

To check, substitute these concentrations into the Equilibrium constant expression,

$$K = \frac{[AB]_{eq}^2}{[A_2]_{eq} [B_2]_{eq}} = \frac{(5.08)^2}{(5.46)(9.46)} = 0.5, \text{ matches up.}$$

Problem 3. Answer: $K_c = \frac{[NO]^4}{[H^+]^4[NO_3^-]^4}$

Solution: Pure solids and pure liquids and solvents are not included in the expression. Products go over Reactants, and coefficients in the equation are written as superscripts.

Problem 4. Solution:

$$K_c = [CO_{2(g)}]$$

Remember: Solids and liquids are not included in the expression.

Problem 5. Solution: Equation 2 is equal the double and reverse of equation 1 therefore

$$K_{p2} = K_{p1}^{-2} = \left(\frac{1}{0.157}\right)^2 = 40.6$$

Problem 6. Answer: Equilibrium Constant = $K_1^{-1/2} = \frac{1}{\sqrt{K_1}}$

Solution: The second equation if reversed (1/K) and halved (K1/2). Combining these two gives 1/K1/2.

Problem 7. Answer: The reaction equation is:



The relationship between K_c and K_p is:

$K_p = K_c(RT)^{\Delta n \text{ gas}}$ In this case there are 3 moles of gas in the reactants and 2 moles of gas in the products, so $\Delta n = -1$

So solving for K_p :

$$K_p = K_c(RT)^{\Delta n \text{ gas}} = (3.3 \times 10^{91}) \left[\left(0.0821 \frac{\text{L atm}}{\text{mol K}} \right) (298 \text{ K}) \right]^{-1} = 1.35 \times 10^{90}$$

Problem 8. Solution:

	$\text{N}_{2(g)} +$	$\text{C}_2\text{H}_2(g) \rightleftharpoons$	$2 \text{HCN}_{(g)}$
i:	1.00	1.00	1.00
c:	+x	+x	-2x
e:	1.00+x	1.00+x	1.00-2x

$\Rightarrow Q=1>K$ so then rxn goes to the left

$$\frac{(1.00-2x)^2}{(1.00+x)^2} = K_c \Rightarrow \frac{(1.00-2x)}{(1.00+x)} = \sqrt{K_c}$$

$$x = \frac{1 - \sqrt{K_c}}{2 + \sqrt{K_c}} = 0.488$$

Problem 9. Solution:

	$\text{COCl}_2(g)$	$\rightleftharpoons \text{CO}_{(g)}$	$+ \text{Cl}_2(g)$
initial:	0.04	0	0
change:	-x	+x	+x
equil:	0.04-x	x	x

$$K_c = \frac{x^2}{0.04-x}$$

$$x^2 + K_c x - 0.04 K_c = 0$$

$$x = \frac{-K_c + \sqrt{K_c^2 - (4)(0.04)(K_c)}}{2} = 5.29 \times 10^{-3}$$

Problem 10. Solution: $K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} = 5.10$

	CO +	H ₂ O ⇌	CO ₂	+H ₂
I	0.1M	0.1	0.1	0.1
C	-x	-x	+x	+x
E	0.1-x	0.1-x	0.1+x	0.1+x

$$K_c = \frac{(0.1+x)^2}{(0.1-x)^2} = \frac{0.01+0.2x+x^2}{0.01-0.2x+x^2} = 5.10$$

$$0.01+0.2x+x^2 = 0.051-1.02x+x^2$$

$$0 = 0.041 - 1.22x$$

$$1.22x = 0.041$$

$$x = 0.034M$$

Therefore, at equilibrium $[H_2] = 0.1 + x = 0.1 + 0.034M = 0.134M$

Problem 11. Solution: Only C is true

An increase in volume will shift the equilibrium to the right thus causing an increase in the total moles of CO at equilibrium.

Problem 12. Solution:

- a) shift to the left
- b) no effect
- c) shift to the right
- d) shift to the right

Problem 13. Solution:

The reaction will shift left forming Ni(CO)_{4(g)} to reach equilibrium

Problem 14. Answer: C

$$\text{Solution: } Q = \frac{[NO]^2[Cl_2]}{[NOCl]^2} = \frac{(1.2)^2(0.56)}{(1.3)^2} = 0.51. \quad Q=K, \text{ therefore we are already at equilibrium.}$$

Solutions to Acids and Bases Practice Problems

Problem 15. Solution: Equal volumes of 0.1 M NaF and 0.1 M HF

Adding an acid and the salt of its conjugate base can form a buffer, this is the case in (b).

Problem 16. Solution: 1 and 3.

A buffer normally consists of a weak acid and its conjugate base in roughly equal amounts. The ratio should be no greater than 0.1 to 10 of weak base to weak acid. In 1, the ratio of acid to base is 3:1. In 3 the ratio is 4:1. In 2, there is a greater amount of strong base than acid, so all of the acetic acid is consumed so it is not a buffer. 4 is not a buffer solution since all of the weak acid is consumed with strong base, 5 is not a buffer because sodium acetate is a weak base, so you have a weak base with a strong base in solution.

Problem 17. Solution: B

This is a buffer solution, therefore:

$$pH = pK_a + \log \left\{ \frac{[A^-]_{eq}}{[HA]_{eq}} \right\} = -\log(1.20 \times 10^{-2}) + \log \left\{ \frac{0.400}{0.600} \right\} = 1.74$$

Problem 18. Solution: This is a buffer solution, therefore:

$$pH = pK_a + \log \left\{ \frac{[A^-]_{eq}}{[HA]_{eq}} \right\} = 4.75 + \log \left\{ \frac{[CH_3COONa]}{0.100} \right\} = 4.75$$

$$\text{Therefore } \log \left\{ \frac{[CH_3COONa]}{0.100} \right\} = 0 \text{ and } \left\{ \frac{[CH_3COONa]}{0.100} \right\} = 1$$

$$[CH_3COONa] = 0.10M$$

$$\# \text{ moles } CH_3COONa = 0.10 \text{ moles}$$

Problem 19. Solution: For this equilibrium $[H^+] = [In^-] = 10^{-8} = 1 \times 10^{-8}$

$$K_a = 1 \times 10^{-6} = \frac{[H^+][In^-]}{[HIn]} = \frac{(1 \times 10^{-8})^2}{[HIn]}$$

$$[HIn] = 1 \times 10^{-10}, \text{ therefore } [HIn]/[In^-] = 1 \times 10^{-10}/1 \times 10^{-8} = 0.01 = 1/100$$

Problem 20. Solution: pH = 8.91

$$\begin{aligned} \text{pH} &= \text{pKa} + \log \frac{\text{CN}^-}{\text{HCN}} \\ &= 9.20 + \log \frac{1.0}{2.0} \\ &= 8.91 \end{aligned}$$

Problem 21. Solution: C

This is a buffer system as there are equal amounts of conjugate acid and base, but the addition of H⁺ can change the pH slightly. The original pH of the buffer is approximately equal to pKa. When H⁺ ions are added from the strong acid HCl, A⁻ is converted into HA. Therefore the addition of 0.01 moles H⁺ produces 0.01 moles HA and consumes 0.01 moles A⁻.

$$n\text{HA} = 0.5 + 0.01 = 0.51 \text{ mol}$$

$$n\text{A}^- = 0.5 - 0.01 = 0.49 \text{ mol}$$

$$[\text{H}^+] = K_a \times n\text{HA}/n\text{A}^- = (1.8 \times 10^{-4}) (0.51/0.49) = 1.873 \times 10^{-4}$$

$$\text{pH} = -\log (1.873 \times 10^{-4}) = 3.727$$

Problem 22. Solution: C

There are more moles of carbonate buffer in solution c than any of the other solutions

Problem 23. Solution: E

The solution is a buffer with pH above 7. A buffer is resistant to both addition of strong acid and strong base and the concentration of the hydronium ion is not more than the hydroxide ion (pH >7).

Problem 24. Solution: E

	HCN +	H ₂ O ⇌	CN ⁻ +	H ₃ O ⁺
I	0.5		y	0
C	-1 × 10 ⁻⁷		+1 × 10 ⁻⁷	+1 × 10 ⁻⁷
E	0.5		y + 1 × 10 ⁻⁷	+1 × 10 ⁻⁷

$$K_a = 6.2 \times 10^{-10} = [(1 \times 10^{-7})(Y + 1 \times 10^{-7})] / 0.5$$

$$Y = 0.003\text{M} \times 1\text{L} = 0.003\text{moles}$$

$$\text{Mass} = 49.0075\text{g/mol NaCN} \times 0.003 \text{ moles} = 0.15\text{g}$$

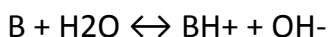
Problem 25. Solution: E

A buffer normally consists of a weak acid and its conjugate base in roughly equal amounts. The ratio should be no greater than 0.1 to 10 of weak base to weak acid. In 1, the ratio of acid to base is 3:1. In 3 the ratio is 4:1. In 2, there is a greater amount of strong base than acid.

Problem 26. Solution: C or E

In order to determine which solutions are able to act as buffer solutions, determine what ions will be found in the solution and whether those ions are acidic, basic or spectator ions. If acidic and/or basic ions are found, calculate the amount of ions that are present. For solution A) all ions present (H^+ , NO_3^- , and Na^+) are spectator ions. No buffer abilities possible. For solution B) all ions present (Na^+ , OH^- and Cl^-) are spectator ions. No buffer abilities possible. For solution C) This is a 1:1 ratio of conjugate acid to its conjugate base. This IS a buffer. For solution D) the HCl completely dissociates to form H^+ and Cl^- ions. NH_3 can form an equilibrium where $\text{NH}_3 + \text{H}^+ \leftrightarrow \text{NH}_4^+$. However, HCl and its dissociated ions are present in 0.01mol amounts—the same as the amount of NH_3 . Therefore, all the NH_3 is “used up” in reacting with the HCl , so no buffering abilities are possible. For solution E) the NaOH completely dissociates to form Na^+ and OH^- ions. The 0.004mol of OH^- will react with the 0.01mol of HF to form 0.004mol of F^- and have 0.006mol left of HF since the OH^- is the limiting reagent. This means we have HA and A^- both present in a ratio of 3:2. This is a buffer.

Problem 27. Solution: C



Calculate from the given pH, the concentration of OH^- ions that dissociate form from the reaction of the base with water.

$$\text{pOH} = 14 - \text{pH} = 14 - (8.88) = 5.12$$

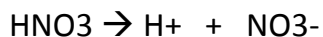
$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-5.12} = 7.585 \times 10^{-6}\text{M}$$

Assume 1 L of solution, therefore the $[\text{B}] = 0.40\text{mol/L}$ and $[\text{BH}^+] = 0.250\text{mol/L}$.

$$K = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} = \frac{(0.250)(7.585 \times 10^{-6})}{0.40} = 4.74 \times 10^{-6}$$

Problem 28. Solution: D

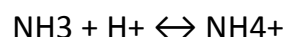
Because equal volumes of the acid and weak base are being mixed, all concentrations (M) can be treated as moles (mol). HNO₃ is a strong acid so it completely dissociates



0.1 0.1 0.1

NH₃ will react with the H⁺ released by the HNO₃ to form NH₄⁺. Initially there is 0.3M or 0.3moles of NH₃. Upon addition of 0.1moles H⁺ (from the HNO₃), 0.1mol of NH₃ will react to form 0.1mol of NH₄⁺, leaving 0.2mol NH₃ unreacted.

Therefore,



Using the following equation, solve for [H⁺].

$$[\text{H}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]}$$

[A⁻]

$$K_w = K_a \times K_b \text{ so that } K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

$$K_b = 1.8 \times 10^{-5}$$

$$[\text{H}^+] = 5.56 \times 10^{-10} \times \frac{[0.1]}{[0.2]} = 2.78 \times 10^{-10} \text{M}$$

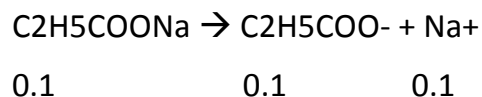
[0.2]

$$\text{pH} = -\log[\text{H}^+] = -\log[2.78 \times 10^{-10}] = 9.56$$

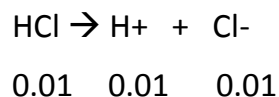
Problem 29. Solution: B

Write out the equations that are occurring in the solution described above. Because both solutes are being added to 1L of water, all concentrations (M) can be treated as moles (mol).

C₂H₅COONa is a soluble salt so it completely dissociates



HCl is a strong acid so it completely dissociates



C₂H₅COO⁻ will react with all the H⁺ to form C₂H₅COOH. Initially there is 0.1 mole of C₂H₅COO⁻. When 0.01mol of H⁺ is added, the C₂H₅COO⁻ reacts leaving 0.09mol. There is also 0.1mol of C₂H₅COOH to start, but when the C₂H₅COO⁻ reacts with the H⁺, it forms 0.01mol more C₂H₅COOH so that the total amount of C₂H₅COOH is 0.11mol.



Before HCl is added 0.1 0.1

After HCl is added 0.11 0.09

Calculate [H⁺] using the following equation. (n = moles)

$$[\text{H}^+] = K_a \times \frac{n_{\text{HA}}}{n_{\text{A}^-}} = 1.41 \times 10^{-5} \times \frac{0.11}{0.09} = 1.72 \times 10^{-5} \text{M}$$

Calculate pH from the [H⁺].

$$\text{pH} = -\log[\text{H}^+] = -\log[1.72 \times 10^{-5}] = 4.76$$

Solutions to Kinetics Practice Problems

Problem 30. Solution:

$$\frac{v_1}{v_2} = \frac{k[I^-]_1^m [S_2O_8^{2-}]_1^n}{k[I^-]_2^m [S_2O_8^{2-}]_2^n}$$

$$\frac{1.25 \times 10^{-5}}{6.25 \times 10^{-6}} = \frac{k(0.080)^m (0.040)^n}{k(0.040)^m (0.040)^n} = 2 = 2^m \Rightarrow m = 1$$

$$\frac{v_1}{v_3} = \frac{1.25 \times 10^{-5}}{6.25 \times 10^{-6}} = \frac{k(0.080)^m (0.040)^n}{k(0.080)^m (0.020)^n} = 2 = 2^n \Rightarrow n = 1$$

$$\text{rate} = k[I^-]^1 [S_2O_8^{2-}]^1$$

$$k = \frac{\text{rate}}{[I^-][S_2O_8^{2-}]}$$

$$k_1 = \frac{1.25 \times 10^{-5}}{(0.080) \cdot (0.040)} = 3.91 \times 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$$

Problem 31. Solution:

$$\text{Rate} = k[\text{H}_2\text{O}]^x [\text{CH}_3\text{Cl}]^y$$

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k(0.0100)^x}{k(0.0200)^x} = \frac{3.6 \times 10^{-4}}{1.44 \times 10^{-4}}$$

$0.5x = .25$, therefore $x = 2$ and the reaction is second-order in H_2O

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k(0.0100)^x}{k(0.0200)^x} = \frac{3.6 \times 10^{-4}}{1.44 \times 10^{-4}}$$

$$5.54 \left(\frac{2}{3}\right)^y = 3.69$$

$\left(\frac{2}{3}\right)^y = \frac{2}{3}$, therefore $y = 1$ and the reaction is first-order in CH_3Cl

$$\text{Rate} = k[\text{H}_2\text{O}]^2 [\text{CH}_3\text{Cl}]^1$$

Problem 32. Solution

$$\ln[A]_{t_{1/2}} = \ln[A]_0 - kt_{1/2}, \quad \ln\left(\frac{[A]_0}{[A]_{t_{1/2}}}\right) = kt_{1/2}$$

$$\text{for } t_{1/2} \quad [A]_{t_{1/2}} = \frac{[A]_0}{2}$$

$$\ln\left(\frac{[A]_0}{[A]_{t_{1/2}}}\right) = \ln\left(\frac{[A]_0}{[A]_0/2}\right) = \ln 2 = kt_{1/2}$$

$$\Rightarrow t_{1/2} = \frac{\ln(2)}{k}$$

Problem 33. Solution: If 20% decomposes, then 80% of the sample remains.

$$\ln[A] = \ln[A]_0 - kt \quad \text{rearrange}$$

$$\ln\left(\frac{0.8[A]_0}{[A]_0}\right) = -k(50s)$$

$$k = 4.463 \times 10^{-3} \text{ sec}^{-1}$$

$$t_{1/2} = \frac{\ln 2}{k} = 155 \text{ sec}$$

Problem 34. Solution: (a)

$$\frac{v_1}{v_2} = \frac{k[\text{CH}_3\text{NNCH}_3]_1^n}{k[\text{CH}_3\text{NNCH}_3]_2^n}$$

$$\frac{2.8 \times 10^{-6}}{1.1 \times 10^{-5}} = \frac{(5.13 \times 10^{-2})^n}{(2.05 \times 10^{-1})^n} = 0.25 = 0.25^n \Rightarrow n = 1$$

Therefore, the reaction is the first order.

$$\text{Rate} = k [\text{CH}_3\text{NNCH}_3(\text{g})], \text{ therefore } k = \frac{2.8 \times 10^{-6} \text{ M/s}}{5.13 \times 10^{-2} \text{ M}} = 5.46 \times 10^{-5} \text{ s}^{-1}$$

$$(b) \quad \ln[A]_t = \ln[A]_0 - kt$$

$$\ln[0.1 - 5.13 \times 10^{-2}] = \ln[5.13 \times 10^{-2}] - (5.46 \times 10^{-5}) \times t$$

$$-5.27 = -2.97 - (5.46 \times 10^{-5}) \cdot t$$

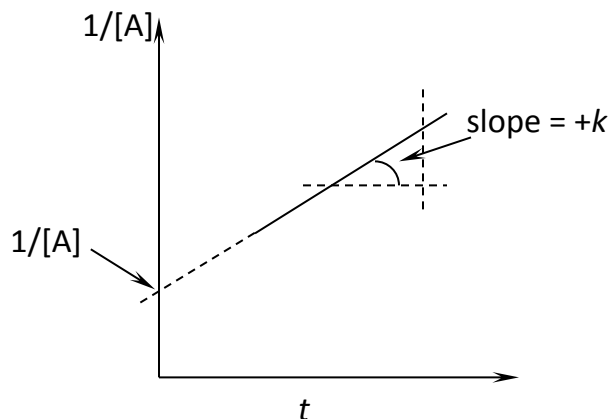
$$(5.46 \times 10^{-5}) \cdot t = 2.30$$

$$t = 4.21 \times 10^4 \text{ s} = 11.7 \text{ hours}$$

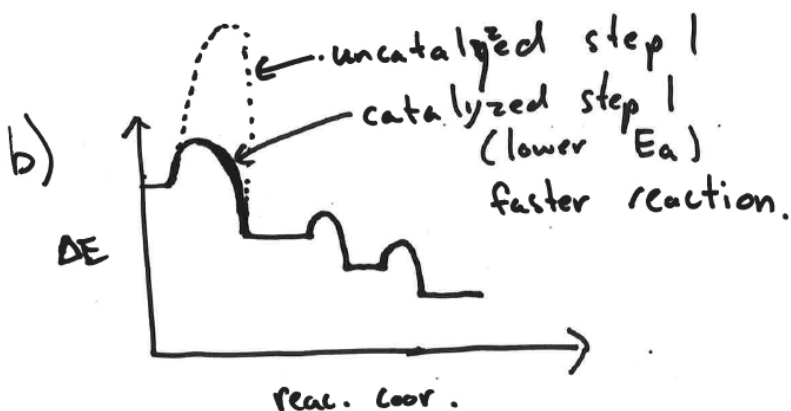
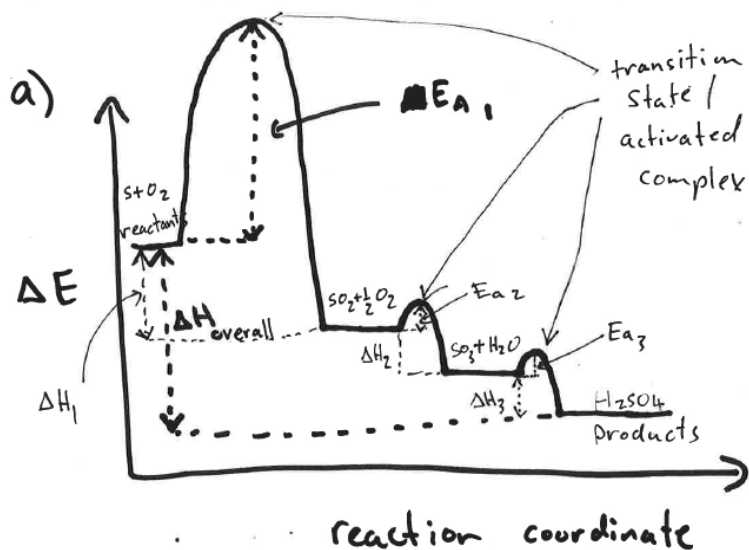
$$(c) \quad [A]_{10\%} = 0.1 \cdot 5.13 \times 10^{-2} = 5.12 \times 10^{-3} \text{ M}$$

$$\text{Rate} = k[A] = (5.46 \times 10^{-5} \text{ s}^{-1})(5.12 \times 10^{-3} \text{ M}) = 2.80 \times 10^{-7} \text{ M/s}$$

Problem 35. Solution: Because this reaction is second order $\frac{1}{[A]} - \frac{1}{[A]_0} = kt$ if $1/[A]$ was plotted vs. t then the y-intercept would be $1/[A]_0$ and the slope would be k



Problem 36. Answer



Problem 37. Solution: Since $\Delta H_{rxn} > 0$, then $\Delta H_{products} > \Delta H_{reactants}$

Thus, $E_a \text{ rev} = 66 - 41 = 25 \text{ kJ/mol}$

(draw an energy diagram to see this better)

Problem 38. Solution:

Let $T_1 = 96^\circ\text{C} = 369 \text{ K}$, and $T_2 = 25^\circ\text{C} = 298 \text{ K}$.

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

$$\ln\left(\frac{3.55 \times 10^{10} \text{ s}^{-1}}{1.2 \times 10^{10} \text{ s}^{-1}}\right) = -\frac{E_a}{8.314 \text{ JK}^{-1} \text{ mol}^{-1}} \left(\frac{1}{369 \text{ K}} - \frac{1}{298 \text{ K}}\right)$$

and solve for E_a , $E_a = 12.8 \text{ kJ/mol}$

Problem 39. Solution: from Arrhenius equation $\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

since $v \propto k$, then

$$\ln\left(\frac{k_2}{k_1}\right) = \ln\left(\frac{v_2}{v_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln(3) = -\frac{E_a}{8.314} \left(\frac{1}{325} - \frac{1}{313}\right) \Rightarrow E_a = 77433.3 \text{ J/mol} = 77.4 \text{ kJ/mol}$$

Problem 40. Solution: Since we have an elementary process, then rate of the reaction is $\text{rate} = k[A]^2$,

This reaction is second order therefore $\frac{1}{[A]} - \frac{1}{[A]_0} = kt$

$$\frac{1}{0.1 \text{ M}} - \frac{1}{0.2 \text{ M}} = k(35.2 \text{ min})$$

$$5 \text{ M}^{-1} = k \cdot (35.2 \text{ min})$$

$$k = 1.42 \times 10^{-1} \text{ M}^{-1} \cdot \text{min}^{-1}$$

Problem 41. The steps are elementary, and the first step is the rate determining step. So the overall rate law only depends on the first step:

$$\text{rate} = k[\text{O}_3][\text{NO}]$$

