

Exam 3 solubility review problems

72. Calculate the solubility of each of the following compounds in moles per liter. Ignore any acid-base properties. Determine the concentration of each ion in each solution.
- PbI_2 , $K_{sp} = 1.4 \times 10^{-8}$
 - CdCO_3 , $K_{sp} = 5.2 \times 10^{-12}$
 - $\text{Sr}_3(\text{PO}_4)_2$, $K_{sp} = 1 \times 10^{-31}$

74. Use the following data to calculate the K_{sp} value for each solid.

- The solubility of $\text{Pb}_3(\text{PO}_4)_2$ is 6.2×10^{-12} mol/L.
- The solubility of Li_2CO_3 is 5.47 g/L.

75. For each of the following pairs of solids, determine which solid has the smallest molar solubility.

- $\text{CaF}_2(s)$, $K_{sp} = 4.0 \times 10^{-11}$ or $\text{BaF}_2(s)$, $K_{sp} = 2.4 \times 10^{-5}$
- $\text{Ca}_3(\text{PO}_4)_2(s)$, $K_{sp} = 1.3 \times 10^{-32}$ or $\text{FePO}_4(s)$, $K_{sp} = 1.0 \times 10^{-22}$

76. The K_{sp} for silver sulfate (Ag_2SO_4) is 1.2×10^{-5} . Calculate the solubility of silver sulfate in each of the following.

- water
- 0.10 M AgNO_3
- 0.20 M K_2SO_4

77. Calculate the solubility (in mol/L) of $\text{Fe}(\text{OH})_3$ ($K_{sp} = 4 \times 10^{-38}$) in each of the following.

- a solution buffered at pH = 5.0
- a solution buffered at pH = 11.0

78. The solubility of $\text{Ce}(\text{IO}_3)_3$ in a 0.20 M KIO_3 solution is 4.4×10^{-8} mol/L. Calculate K_{sp} for $\text{Ce}(\text{IO}_3)_3$.

81. Will a precipitate form when 100.0 mL of 4.0×10^{-4} M $\text{Mg}(\text{NO}_3)_2$ is added to 100.0 mL of 2.0×10^{-4} M NaOH ?

82. A solution is prepared by mixing 75.0 mL of 0.020 M BaCl_2 and 125 mL of 0.040 M K_2SO_4 . K_{sp} for $\text{BaSO}_4 = 1.1 \times 10^{-10}$. Does a precipitate form? If so, how many grams of precipitate are formed?

(Zumdahl, Chemical Principles, 5th Edition)

76a) in pure water $K_{sp} = 4x^3$
 $x = 1.44 \times 10^{-2}$

b) with a common ion, use K_{sp} expression:

$$K_{sp} = [\text{Ag}^+]^2 [\text{SO}_4^{2-}]$$

$$1.2 \times 10^{-5} = (.1)^2 [\text{SO}_4^{2-}]$$

$$[\text{SO}_4^{2-}] = 1.2 \times 10^{-3} \text{ M}$$

since one Ag_2SO_4 produces one SO_4^{2-} , $[\text{SO}_4^{2-}] = \text{molar solubility}$.

c) $K_{sp} = [\text{Ag}^+]^2 [0.20]$ $[\text{Ag}^+] = 7.75 \times 10^{-3}$
 $[\text{Ag}^+] = 2x$, so molar solubility = 3.87×10^{-3} M.

72a $K_{sp} = 4x^3$
 $x = 1.52 \times 10^{-3} \text{ M}$ $[\text{Pb}^{2+}] = x$
 $[\text{Pb}^{2+}] = 1.52 \times 10^{-3} \text{ M}$ $[\text{I}^-] = 2x$
 $[\text{I}^-] = 3.04 \times 10^{-3} \text{ M}$

b $K_{sp} = x^3$
 $x = 2.28 \times 10^{-6} \text{ M}$
 $[\text{Cd}^{2+}] = [\text{CO}_3^{2-}] = 2.28 \times 10^{-6}$

c. $K_{sp} = 108x^5$
 $x = 2.47 \times 10^{-7} \text{ M}$
 $[\text{Sr}^{2+}] = 3x = 7.42 \times 10^{-7} \text{ M}$
 $[\text{PO}_4^{3-}] = 2x = 4.95 \times 10^{-7} \text{ M}$

74 a $K_{sp} = 108x^5$ $x = 6.2 \times 10^{-12}$
 $K_{sp} = 9.89 \times 10^{-55}$

b $5.47 \frac{\text{g}}{\text{L}} \times \frac{1 \text{ mol}}{73.8 \text{ g}} = .0741 \text{ M}$

$$K_{sp} = 4x^3 = 4(.0741)^3$$

$$K_{sp} = 1.63 \times 10^{-3}$$

75a - both are 1:2 ion ratio, so compare K_{sp} directly. CaF_2 has smaller K_{sp} , so smaller solubility.

b - $\text{Ca}_3(\text{PO}_4)_2$ $K_{sp} = 108x^5$
 $x = 1.64 \times 10^{-7}$

$$\text{FePO}_4 \text{ } K_{sp} = x^2$$

$$x = 1 \times 10^{-11}$$

FePO_4 has smaller molar solubility.

77 a) $[H^+] = 10^{-5}$, so $[OH^-] = 10^{-9}$

$K_{sp} = [Fe^{3+}][OH^-]^3$ $[Fe^{3+}] = 4 \times 10^{-11} M$ molar solubility = $4 \times 10^{-11} M$

b) $[H^+] = 10^{-11}$, so $[OH^-] = 10^{-3}$

$K_{sp} = [Fe^{3+}][OH^-]^3$ $[Fe^{3+}] = 4 \times 10^{-29} M$ molar solubility = $4 \times 10^{-29} M$

78 molar solubility = $x = 4.4 \times 10^{-8} M = [Ce^{3+}]$

$K_{sp} = [Ce^{3+}][IO_3^-]^3 = (4.4 \times 10^{-8})(.2)^3 = 3.52 \times 10^{-10}$

81 calculate concentrations in mixed solution, then calculate Q_{sp}

$[Mg^{2+}] = \frac{M \times V}{total V} = \frac{(1L)(4 \times 10^{-4} M)}{(1L) + (1L)} = 2 \times 10^{-4} M$

$[OH^-] = \frac{(2L)(2 \times 10^{-4} M)}{0.2L} = 1 \times 10^{-4} M$

K_{sp} is not given in the problem - Google it! 5.61×10^{-12}

$Q_{sp} = [Mg^{2+}][OH^-]^2 = (2 \times 10^{-4})(1 \times 10^{-4})^2 = 2 \times 10^{-12}$

$Q_{sp} < K_{sp}$, so no precipitate forms.

82 $[Ba^{2+}] = \frac{(0.75L) \times (0.20M)}{0.20L} = 7.5 \times 10^{-3} M$

$[SO_4^{2-}] = \frac{(0.125L) \times (0.040M)}{0.20L} = 2.5 \times 10^{-2} M$

$Q_{sp} = (7.5 \times 10^{-3})(2.5 \times 10^{-2}) = 1.88 \times 10^{-4} M$ $K_{sp} = 1.1 \times 10^{-10}$

$Q_{sp} > K_{sp}$, so a precipitate forms.

Look at MOLES of each ion present:

$Ba^{2+}: .075L \times .020M = 1.5 \times 10^{-3} \text{ moles}$

$SO_4^{2-}: .125L \times .04M = 5 \times 10^{-3} \text{ moles}$

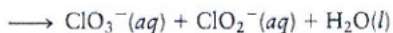
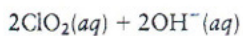
They will react until one of them is used up.

$1.5 \times 10^{-3} \text{ moles } Ba^{2+} \rightarrow 1.5 \times 10^{-3} \text{ moles } BaSO_4$

$1.5 \times 10^{-3} \text{ mol } BaSO_4 \times \frac{233.4g}{1 \text{ mol}} = 0.35g BaSO_4$

Exam 3 kinetics review problems

19. The following data were obtained for the reaction



	$[\text{ClO}_2]_0$ (mol/L)	$[\text{OH}^-]_0$ (mol/L)	Initial Rate (mol L ⁻¹ s ⁻¹)
1	0.0500	0.100	5.75×10^{-2}
2	0.100	0.100	2.30×10^{-1}
3	0.100	0.0500	1.15×10^{-1}

- Determine the rate law and the value of the rate constant.
- What would be the initial rate for an experiment with $[\text{ClO}_2]_0 = 0.175 \text{ mol/L}$ and $[\text{OH}^-]_0 = 0.0844 \text{ mol/L}$?

(Zumdahl, Chemical Principles, 5th Edition)

- What is the activation energy for a reaction if its rate constant is found to triple when the temperature is raised from 600. K to 610. K?
- For a gas-phase reaction, the pre-exponential factor A is 45.38 and the rate constant is 0.0850 min^{-1} at 273 K. Find the rate constant at 323 K.
- The rate constant of a reaction is tripled when the temperature is increased from 298 K to 308 K. Find E_a .

(Whitten, Davis, Peck, and Stanley, Chemistry, 8th Edition.)

55. Calculate E_a using the single-temperature Arrhenius equation, then use that in the two-temperature Arrhenius equation to solve for K_2

$$k = A e^{-E_a/RT}$$

$$\ln k = \ln A - E_a/RT$$

$$-RT(\ln k - \ln A) = E_a$$

$$(-8.314)(273)(\ln(0.0850) - \ln(45.38)) = E_a$$

$$E_a = 14,254 \text{ J/mol}$$

next column →

19.a) rate = $k [\text{ClO}_2]^x [\text{OH}^-]^y$

compare trials 1 and 2:

$$\left[\frac{.1}{.05}\right]^x = \left[\frac{0.230}{0.0575}\right]$$

$$[2]^x = [4] \quad x = 2$$

compare trials 2 and 3
doubling $[\text{OH}^-]$ doubles the rate. Therefore $y = 1$

$$\text{rate} = k [\text{ClO}_2]^2 [\text{OH}^-]$$

choose any trial, plug in rate, $[\text{ClO}_2]$, and $[\text{OH}^-]$

$$k = 230 \text{ M}^{-2}\text{s}^{-2}$$

b) rate = $230 (.175)^2 (.0844)$
rate = 0.594 M/s

54 $\ln \frac{K_2}{K_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$

$$\ln 3 = \frac{E_a}{8.314} \left(\frac{1}{600} - \frac{1}{610} \right)$$

$$E_a = 335 \text{ kJ/mol}$$

56 - just like 54, but

$$T_1 = 298 \text{ and } T_2 = 308$$

$$E_a = 83,834 \text{ J/mol}$$

$$\ln \frac{K_2}{K_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\frac{K_2}{K_1} = e^{\frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)}$$

$$\frac{K_2}{K_1} = e^{.972}$$

$$K_2 = K_1 \times 2.64$$

$$K_2 = 0.224 \text{ min}^{-1}$$

42. Define each of the following.
- a. elementary step - a single step in a multi-step reaction, or a reaction that occurs in only one step.
 - b. reaction mechanism - the step by step process through which a reaction occurs.
 - c. rate-determining step - the slowest elementary step in a mechanism.

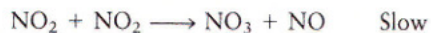
Write the rate laws for the following elementary reactions.

- a. $\text{CH}_3\text{NC}(g) \longrightarrow \text{CH}_3\text{CN}(g)$ rate = $k[\text{CH}_3\text{NC}]$
- b. $\text{O}_3(g) + \text{NO}(g) \longrightarrow \text{O}_2(g) + \text{NO}_2(g)$ rate = $k[\text{O}_3][\text{NO}]$
- c. $\text{O}_3(g) \longrightarrow \text{O}_2(g) + \text{O}(g)$ rate = $k[\text{O}_3]$
- d. $\text{O}_3(g) + \text{O}(g) \longrightarrow 2\text{O}_2(g)$ rate = $k[\text{O}_3][\text{O}]$
- e. $^{14}_6\text{C} \longrightarrow ^{14}_7\text{N} + \beta \text{ particle (nuclear decay)}$

rate = $k[\text{O}_3]$

rate laws for elementary reactions CAN include intermediates. But not for overall reactions.

43. The mechanism for the reaction of nitrogen dioxide with carbon monoxide to form nitric oxide and carbon dioxide is thought to be

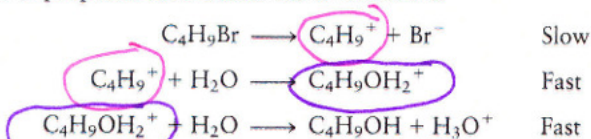


$$\text{rate} = k[\text{NO}_2]^2$$



Write the rate law expected for this mechanism. What is the overall balanced equation for the reaction?

44. A proposed mechanism for a reaction is



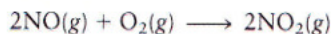
$$\text{rate} = k[\text{C}_4\text{H}_9\text{Br}]$$



45. Write the rate law expected for this mechanism. What is the overall balanced equation for the reaction? What are the intermediates in the proposed mechanism?

Intermediates are circled.

47. The reaction



exhibits the rate law

$$\text{Rate} = k[\text{NO}]^2[\text{O}_2]$$

Which of the following mechanisms is consistent with this rate law?

- a. $\text{NO} + \text{O}_2 \longrightarrow \text{NO}_2 + \text{O}$ Slow rate = $k[\text{NO}][\text{O}_2]$
 $\text{O} + \text{NO} \longrightarrow \text{NO}_2$ Fast
- b. $\text{NO} + \text{O}_2 \rightleftharpoons \text{NO}_3$ Fast equilibrium rate = $k[\text{NO}]^2[\text{O}_2]$
 $\text{NO}_3 + \text{NO} \longrightarrow 2\text{NO}_2$ Slow
- c. $2\text{NO} \longrightarrow \text{N}_2\text{O}_2$ Slow rate = $k[\text{NO}]^2$
 $\text{N}_2\text{O}_2 + \text{O}_2 \longrightarrow \text{N}_2\text{O}_4$ Fast
 $\text{N}_2\text{O}_4 \longrightarrow 2\text{NO}_2$ Fast
- d. $2\text{NO} \rightleftharpoons \text{N}_2\text{O}_2$ Fast equilibrium rate = $k[\text{NO}]^2$
 $\text{N}_2\text{O}_2 \longrightarrow \text{NO}_2 + \text{O}$ Slow
 $\text{O} + \text{NO} \longrightarrow \text{NO}_2$ Fast

64. Draw a rough sketch of the energy profile for each of the following cases.

a. $\Delta E = +10 \text{ kJ/mol}$, $E_a = 25 \text{ kJ/mol}$

b. $\Delta E = -10 \text{ kJ/mol}$, $E_a = 50 \text{ kJ/mol}$

c. $\Delta E = -50 \text{ kJ/mol}$, $E_a = 50 \text{ kJ/mol}$

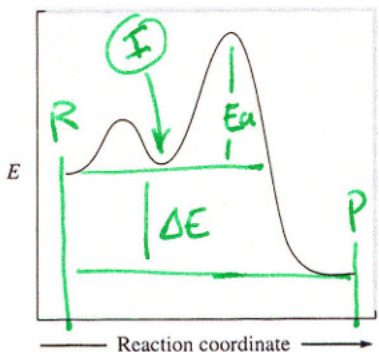
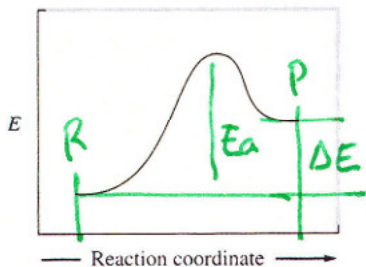
Which reaction will have the greatest rate at 298 K? Assume the frequency factor A is the same for all three reactions.

65. For the following reaction profiles, indicate:

a. the positions of reactants and products

b. the activation energy

c. ΔE for the reaction



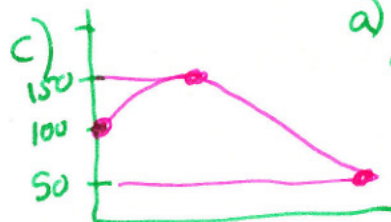
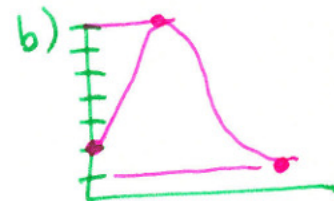
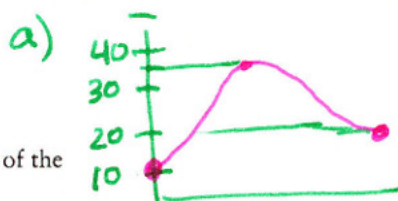
d. The second reaction profile is representative of a reaction that occurs by a two-step mechanism. Which point on the plot represents the energy of the intermediate in the two-step reaction? Which step in the mechanism is rate determining, the first or the second step? Explain.

66. The activation energy for the reaction



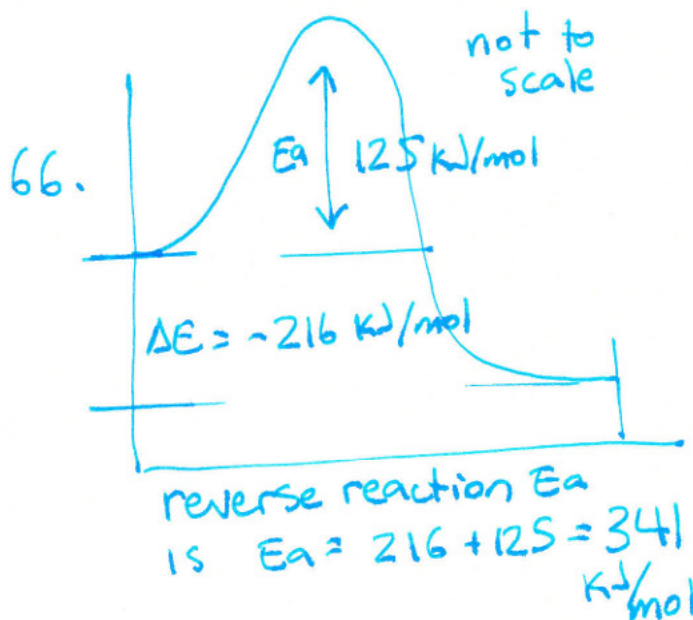
is 125 kJ/mol , and ΔE for the reaction is -216 kJ/mol . What is the activation energy for the reverse reaction $[\text{NO}(\text{g}) + \text{CO}_2(\text{g}) \longrightarrow \text{NO}_2(\text{g}) + \text{CO}(\text{g})]$?

67. For a certain process, the activation energy is greater for the forward reaction than for the reverse reaction. Does this reaction have a positive or negative value for ΔE ?



a) will have the greatest rate (lowest E_a)

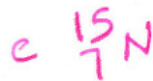
d) the intermediate is at the low point between the two E_a values. peaks The second step is rate limiting because it has a higher E_a .





Exam 3 nuclear review problems

9. In 1994 it was proposed that element 106 be named seaborgium, Sg, in honor of Glenn T. Seaborg, discoverer of the transuranium elements.
- ${}^{263}\text{Sg}$ was produced by the bombardment of ${}^{249}\text{Cf}$ with a beam of ${}^{18}\text{O}$ nuclei. Complete and balance an equation for this reaction.
 - ${}^{263}\text{Sg}$ decays by α -particle emission. What is the other product resulting from the α decay of ${}^{263}\text{Sg}$?
10. Many elements have been synthesized by bombarding relatively heavy atoms with high-energy particles in particle accelerators. Complete the following nuclear reactions, which have been used to synthesize elements.
- $\text{_____} + {}_2^4\text{He} \rightarrow {}_{97}^{243}\text{Bk} + {}_0^1\text{n}$
 - ${}_{92}^{238}\text{U} + {}_6^{12}\text{C} \rightarrow \text{_____} + 6 {}_0^1\text{n}$
 - ${}_{98}^{249}\text{Cf} + \text{_____} \rightarrow {}_{105}^{260}\text{Db} + 4 {}_0^1\text{n}$
 - ${}_{98}^{249}\text{Cf} + {}_{5}^{10}\text{B} \rightarrow {}_{103}^{257}\text{Lr} + \text{_____}$
13. Radioactive copper-64 decays with a half-life of 12.8 days.
- What is the value of k in s^{-1} ?
 - A sample contains 28.0 mg ${}^{64}\text{Cu}$. How many decay events will be produced in the first second? Assume that the atomic mass of ${}^{64}\text{Cu}$ is 64.0.
 - A chemist obtains a fresh sample of ${}^{64}\text{Cu}$ and measures its radioactivity. She then determines that to do an experiment, the radioactivity cannot fall below 25% of the initial measured value. How long does she have to perform the experiment?
17. Phosphorus-32 is a commonly used radioactive nuclide in biochemical research, particularly in studies of nucleic acids. The half-life of phosphorus-32 is 14.3 days. What mass of phosphorus-32 is left from an original sample of 175 mg of $\text{Na}_3{}^{32}\text{PO}_4$ after 35.0 days? Assume that the atomic mass of ${}^{32}\text{P}$ is 32.0.
20. A living plant contains about the same fraction of carbon-14 as atmospheric carbon dioxide. The observed rate of decay of carbon-14 from a living plant is 15.3 counts per minute per gram of carbon. How many counts per minute per gram of carbon will be measured from a 15,000-yr-old sample? Will radiocarbon dating work well for small samples of 10 mg or less?
22. A proposed system for storing nuclear wastes involves storing the radioactive material in caves or deep mine shafts. One of the most toxic nuclides that must be disposed of is plutonium-239, which is produced in breeder reactors and has a half-life of 24,100 years. A suitable storage place must be geologically stable long enough for the activity of plutonium-239 to decrease to 0.1% of its original value. How long is this period for plutonium-239?



$$13a \quad t_{1/2} = \frac{0.693}{k}$$

$$k = 0.054 \text{ days}^{-1} \\ = 6.3 \times 10^{-7} \text{ s}^{-1}$$

b.

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

rate here is in disintegrations per second, not Molarity per second, so $[\text{Cu}]$ is the total number of atoms.

$$28 \times 10^{-3} \text{ g} \times \frac{1 \text{ mole}}{64 \text{ g}} \times \frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mole}}$$

$$= 2.63 \times 10^{20} \text{ atoms.} = [\text{Cu}]_0$$

$$\text{rate} = k [\text{Cu}]_0$$

$$\text{rate} = (6.3 \times 10^{-7} \text{ s}^{-1})(2.63 \times 10^{20})$$

$$\text{rate} = 1.6 \times 10^{14} \frac{\text{decays}}{\text{sec}}$$

17 Original sample is $\frac{.175 \text{ g Na}_3\text{P}^{32}\text{O}_4}{164.97 \text{ g/mol}} = 1.06 \times 10^{-3} \text{ moles}$

$1.06 \times 10^{-3} \text{ moles} \times 32 \text{ g/mol} = 3.39 \times 10^{-2} \text{ grams } ^{32}\text{P}$
in the sample.

$A = A_0 \left(\frac{1}{2}\right)^x$ where $x = \text{number of half-lives}$

$\frac{35.0 \text{ days}}{14.3 \text{ days/half-life}} = 2.45 \text{ half lives}$

$A = 3.39 \times 10^{-2} \left(\frac{1}{2}\right)^{2.45} = 6.20 \times 10^{-3} \text{ grams.}$
or 6.20 mg out of
the original 33.9 mg
 ^{32}P in the sample

20 $A = A_0 \left(\frac{1}{2}\right)^x$ where $x = \text{number of half-lives}$

$x = \frac{15000 \text{ yrs}}{5730 \text{ yrs/half-life}} = 2.62 \text{ half lives}$

$A = \left(15.3 \frac{\text{counts}}{\text{minute}}\right) \left(\frac{1}{2}\right)^{2.62} = 2.49 \text{ counts per minute.}$
per gram.

If a sample is only 10mg and is 15000 years old,
it would have only $\frac{2.49 \text{ cpm}}{\text{gram}} \times .010 \text{ g} = .025 \text{ counts}$
per minute,
or 40 minutes
between counts.

$$22 \quad A = A_0 \left(\frac{1}{2}\right)^x \quad \text{where } x = \text{number of half lives}$$

$$0.1 = 100 \left(\frac{1}{2}\right)^x$$

$$.001 = \left(\frac{1}{2}\right)^x$$

$$\log(.001) = x \log \frac{1}{2}$$

$$-3 = x (-.30)$$

$$x = 10 \text{ half lives}$$

$$10 \times t_{1/2} = 10 \times 24,100 \text{ years} = 241,000 \text{ years.}$$

EXAMPLE 19.4 Radioactive Decay Kinetics

Plutonium-236 is an alpha emitter with a half-life of 2.86 years. If a sample initially contains 1.35 mg of Pu-236, what mass of Pu-236 is present after 5.00 years?

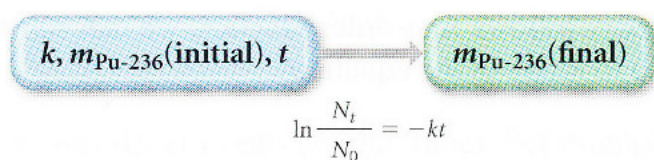
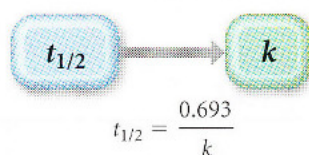
STRATEGY You are given the initial mass of Pu-236 in a sample and asked to find the mass after 5.00 years.

GIVEN: $m_{\text{Pu-236}}(\text{initial}) = 1.35 \text{ mg}$;
 $t = 5.00 \text{ yr}$; $t_{1/2} = 2.86 \text{ yr}$

FIND: $m_{\text{Pu-236}}(\text{final})$

STRATEGIZE Use the integrated rate law (Equation 19.3) to solve this problem. To do so, you must determine the value of the rate constant (k) from the half-life expression (Equation 19.1).

CONCEPTUAL PLAN



Find the value of the rate constant, the initial mass of Pu-236, and the time along with integrated rate law to find the final mass of Pu-236. Since the mass of the Pu-236 ($m_{\text{Pu-236}}$) is directly proportional to the number of atoms (N), and since the integrated rate law contains the ratio (N_t/N_0), the initial and final masses can be substituted for the initial and final number of atoms.

EXECUTE Follow your plan. Begin by finding the rate constant from the half-life.

SOLUTION

$$t_{1/2} = \frac{0.693}{k}$$
$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.86 \text{ yr}}$$
$$= 0.2423/\text{yr}$$

Use the integrated rate law for N_t and substitute the values for the rate constant, the initial mass of Pu-236, and the time into the solved equation. Calculate the final mass of Pu-236.

$$\ln \frac{N_t}{N_0} = -kt$$
$$\frac{N_t}{N_0} = e^{-kt}$$
$$N_t = N_0 e^{-kt}$$
$$N_t = 1.35 \text{ mg} [e^{-(0.2423/\text{yr})(5.00 \text{ yr})}]$$
$$N_t = 0.402 \text{ mg}$$

CHECK The units of the answer (mg) are correct. The magnitude of the answer (0.402 mg) is about one-third of the original mass (1.35 mg) which seems reasonable given that the amount of time is between one and two half-lives. (One half-life would result in one-half of the original mass and two half-lives would result in one-fourth of the original mass.)

PRACTICE 19.4

How long will it take for the 1.35-mg sample of Pu-236 in Example 19.4 to decay to 0.100 mg?