ANSWERS TO UNIT I : REACTION KINETICS

1. Rate of consumption $= \dfrac{5.0\text{ g}}{150\text{ s}} \times \dfrac{60\text{ s}}{1\text{ min}} = \dfrac{2.0\text{ g}}{\text{min}}$

2. Time $= 45.0\text{ g} \times \dfrac{1\text{ min}}{2.35\text{ g}} = 19.1\text{ min}$

3. Volume of $O_2 = 7.50\text{ min} \times \dfrac{32.5\text{ mL}}{\text{min}} = 244\text{ mL}$

4. (a) OK; moles/second = amount/time
   (b) Not acceptable; this is a "rate" but not "amount/time"
   (c) OK; moles/litre is an amount and (moles/litre)/second = amount/time
   (d) Not acceptable; this is a density or concentration
   (e) OK; millilitres/hour = amount/time
   (f) OK; grams/minute = amount/time

5. Rate of consumption of $O_2 = \dfrac{1.34\text{ mol } H_2O}{\text{min}} \times \dfrac{1\text{ mol } O_2}{2\text{ mol } H_2O} = \dfrac{0.67\text{ mol } O_2}{\text{min}}$

6. (a) The mass is decreasing because $CO_2(g)$ is being lost from the solution.
   (b) Slope = –0.006
   (c) i) unit of rise = g ii) unit of run = s iii) units of slope = g/s
   (d) Expected units for rate = g/s
   (e) The rate of the reaction = the slope of the line = –0.006 g/s (a loss of 0.006 g every second)

7. If the reaction occurred in a closed container, no mass would be lost (conservation of mass). If the $NO_2(g)$ was allowed to escape, the mass decrease would be due to the loss of $NO_2(g)$, NOT the loss of Cu(s). [Incidentally, $NO_2(g)$ is quite soluble in water and not all of the NO_2 produced would escape.]

8. (a) Measure the rate at which the intensity of the blue colour in the solution increases.
   (b) Measure the change in mass of Cu(s) and calculate the rate as the mass of Cu used divided by the time required for the reaction; or measure the change in mass of Ag(s) and calculate the rate as the mass of Ag produced divided by the reaction time; or measure the increase in temperature (the reaction is exothermic) and calculate the rate as the temperature change divided by reaction time.

9. (a) The reaction produces two moles of gas for every two moles of gas used up. Hence the number of moles of gas in the container doesn't change, and the gas pressure doesn't change as the reaction proceeds. (Recall "Avogadro's Hypothesis" from Chem 11: equal volumes of gases at the same temperature and pressure contain the same number of molecules or moles.)

   (b) Rate $= \dfrac{1.2\text{ g HCl}}{120\text{ s}} \times \dfrac{1\text{ mol HCl}}{36.5\text{ g HCl}} = 2.7 \times 10^{-4}\text{ mol HCl/s}$

   (c) Rate (of HCl) $= \dfrac{0.200\text{ L } H_2}{1\text{ min}} \times \dfrac{2\text{ L HCl}}{1\text{ L } H_2} = 0.400\text{ L HCl/min}$

10. Reaction (b) is fastest: a single H^+ is removed from NH_4^+ and added to CO_3^{2-}.

    Reaction (a) is moderately slow: 6 bonds have to be broken and made. An O–O bond and 2 O–H bonds have to be broken; 2 O–H bonds and a second bond in O=O must be made.

    Reaction (c) is very slow: many bonds have to be broken and made. Incidentally ... gasoline does not undergo combustion at ROOM TEMPERATURE; a mixture of gasoline and oxygen can exist indefinitely at room temperature. Of course, if you add HEAT (in the form of a spark or match) then BOOM!

11. Since nothing was changed, other than exchanging one reactant (Li) for another (K), the reaction rate change was due to "the nature of the reactants".

12. Surface area has ***no effect*** on a reaction between two gases because gases will completely interm[illegible] when combined. The intermolecular forces are too weak to make gas molecules clump together. As a result, there is no "surface" inside which one kind of gas is found and outside which the other kind of gas is found. In general, surface area will not be an important factor in **any** homogeneous reaction because of the complete mixing which must exist in a homogeneous mixture. In fact, the concept of a "surface" cannot even be defined for a homogeneous mixture.

13. (a) $Ag^+(aq) + I^-(aq) \longrightarrow AgI(s)$ Aqueous ions react faster than gases.
    (b) $CH_3COOH(aq) + H_2O(l) \longrightarrow CH_3COO^-(aq) + H_3O^+(aq)$ The two liquids form a fast–reacting homogeneous mixture, whereas Fe(s) and water can only react at the surface of the iron.
    (c) $CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$ A liquid and solid are expected to react faster than two solid reactants.
    (d) $C(s, powder) + O_2(g) \longrightarrow CO_2(g)$ A powder has a greater surface area than a solid chunk.
    (e) $H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$ Two aqueous ions react faster than a neutral aqueous molecule and an aqueous ion.

14. Both reactions in (a) are homogeneous (the solid AgI is irrelevant since the REACTANTS are in the same phase in each case).

    The second reaction in (b) is homogeneous because $H_2O(l)$ is liquid water and $CH_3COOH(aq)$ refers to acetic acid dissolved in water.

    Both reactions in (e) are homogeneous.

    Note: In (c) the reaction between Cu(s) and S(s) is NOT homogeneous because Cu and S are different solid "phases" (have different properties depending on where one takes a sample).

15. All factors EXCEPT surface area are important in homogeneous reactions. All factors are important in heterogeneous reactions.

16. (a) Powder the Al(s)
    (b) Increase the temperature
    (c) Reduce the volume of the container, so as to increase the pressure
    (d) Add a catalyst
    (e) Add more $F_2(g)$, keeping the volume constant

17. (a) The concentration of the reactants decreases (reactants are used up)
    (b) The rate decreases
    (c) i) graph B. Initially the [reactants] is high and the [products] is zero. Reactants are used up quickly and products are produced quickly, but toward the end the [reactants] is small so that [reactants] decreases very slowly and [products] increases very slowly (levels off).
    ii) graph C. See the explanation for part i)
    (d) i) graph C. Initially there is a large [reactants] and the rate is high. As the reactants get used up, the rate at which the remaining reactants get used slows down and the rate starts to level off.
    ii) graph C. The rate at which the reactants are used up equals the rate at which the products are made.

18. Using the tangent line drawn to the curve at time = 20 s:

$$\text{Rate} = \text{slope} = \frac{\text{rise}}{\text{run}} = \frac{-0.21\ \text{mol/L}}{42\ \text{s}} = -0.0050\ \text{mol/L·s}.$$

19. (a) −0.11 g/s
    (b) −0.047 g/s
    (c) In (b) there are less reactants, including HCl(aq), which decreases the rate of reaction.

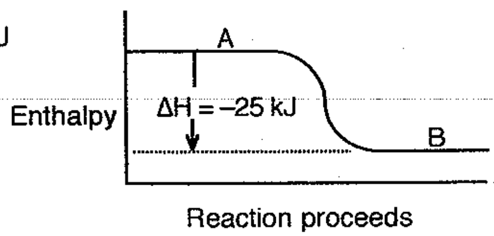
20. If the surface area of reactant A is increased, a given molecule of reactant B has a greater chance of striking a molecule of A so that more collisions can occur between A and B in a specified time. As a result, the reaction rate increases. Molecules of A which are INSIDE a chunk of solid A cannot react; only molecules at the surface can react.

21. (a) Decreases rate. The collisions are less energetic and there are fewer collisions at the lower temperature.
(b) Increases rate. Greater frequency of collisions between O_2 and S.
(c) No effect. Changing the amount of product will not affect the rate of collisions between reactants.
(d) Increases rate. Greater surface area of S exposes more S atoms to collisions with O_2 molecules.
(e) Decreases rate. Increasing the volume decreases the pressure and decreases the $[O_2]$, which decreases the frequency of collisions.

22. Kindling has a larger surface area and therefore a greater frequency of collision between oxygen molecules and the wood.

23. PE must increase (electrons must have sufficient energy to separate from one another and break the bond).

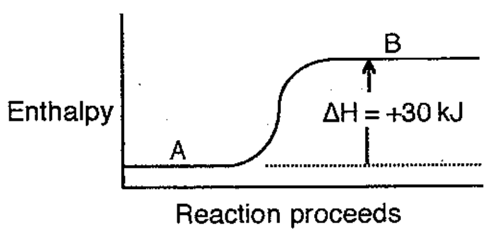
24. $A \longrightarrow B + 25\ kJ$



Since the system of reactants gives off energy to the surroundings, the surroundings feel warmer.

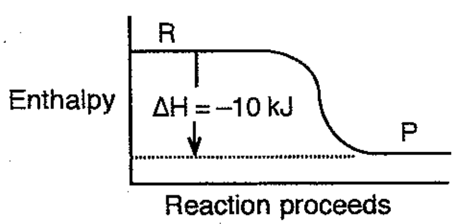
25. $\Delta H = +40\ kJ$

26. $\Delta H = +30\ kJ$. The products have more energy than the reactants.



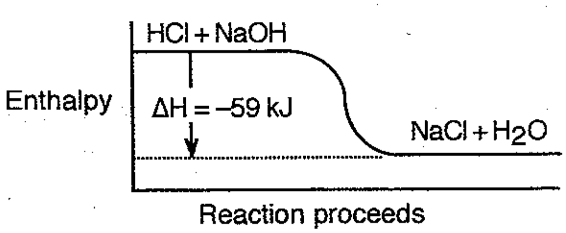
Since the system of reactants absorbs energy from the surroundings, the surroundings feel cooler.

27.



The surroundings will feel warmer.

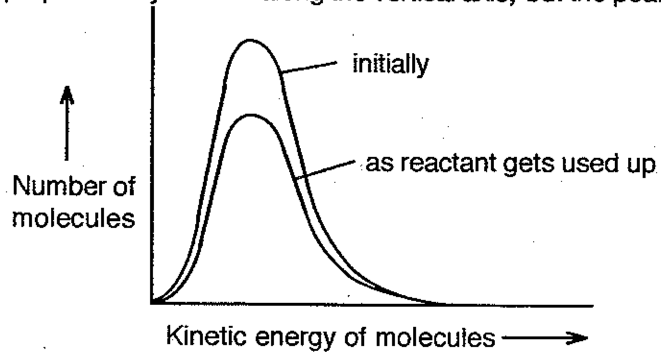
28.



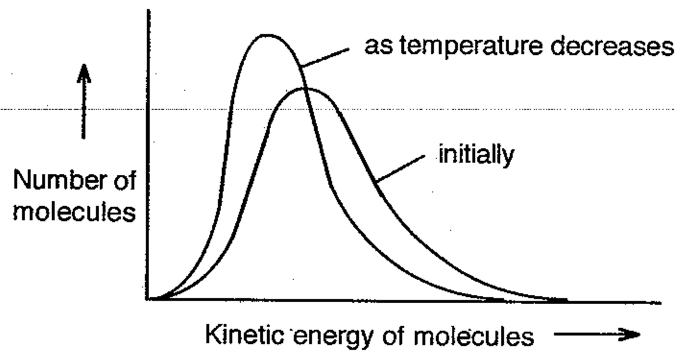
Since heat is absorbed by the surroundings, the system gave off heat.

29. (a) ii
    (b) No, there would be little effect on the rate; the "doubling of rate with a 10°C increase in temperature" rule of thumb ONLY applies to SLOW reactions – this is a fast reaction.

30. (a) The curve is proportionally smaller along the vertical axis, but the peak is still at the same KE value.

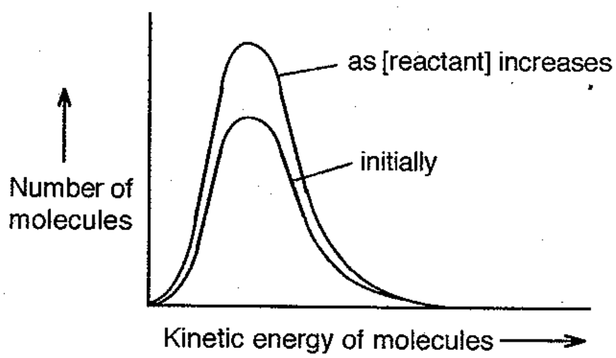


    (b) The peak is at lower KE values, and a bit higher on the vertical axis.



    (c) No effect. Increasing the surface area has no effect on the energies of the molecules; it just makes more molecules available for reaction.

    (d) The overall height of the curve is proportionally larger (a greater concentration of reactants means there will be more molecules at all energies), but the peak is still at the same KE value.

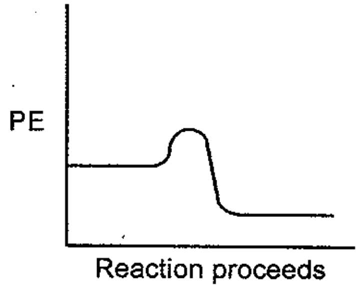


31. Since the rate doubles for every 10°C temperature increase, and since the final temperature is 20°C higher than the original temperature, there are TWO doublings of the rate and the new rate will be:
    $2 \times 2 \times 1.0 \times 10^{-7}$ mol/s = 4.0×10^{-7} mol/s.

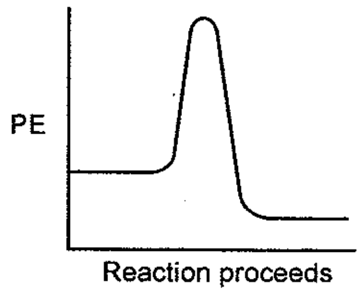
32. Since the temperature has been raised by 30°C, the new rate will be:
$$2 \times 2 \times 2 \times 2.0 \times 10^{-4} \text{ mol/s} = 1.6 \times 10^{-3} \text{ mol/s}.$$

33. The activation energy for the reaction is very large, so that the rate is impossibly slow (luckily).

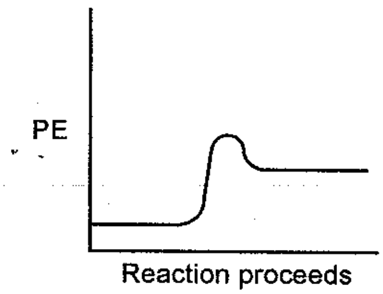
34. (a)



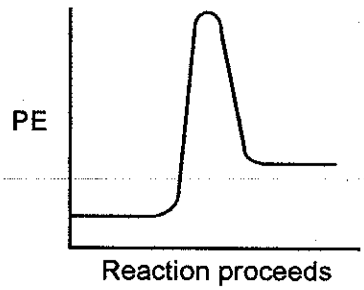
(b)



(c)



(d)



(e) The smaller the hill, the more molecules will have sufficient energy to get over the hill.

35. Not necessarily. Although sufficient KE is available, a favourable geometry is also required.

36. (a) (i) KE decreases: the repulsion of their outer electrons slows down their approach to each other.
(ii) PE increases: the KE lost is gained as PE.
(b) $(KE + PE)_{BEFORE} = (KE + PE)_{AFTER}$; that is, the total energy before equals the total energy after

37. (a) The activation energy would be increased.
(b) The formation of a bond results in the decrease of PE.
(c) exothermic
(d) $A_2 + B_2 \longrightarrow 2\,AB + 70 \text{ kJ}$
(e) $120 - 80 = 40$ kJ

38. The activation energy for the reaction involving F_2 will be less than that for the reaction involving I_2. Because I_2 has more electrons than F_2, it experiences more repulsion from the electrons on the approaching H_2. Overcoming this greater repulsion requires a greater input of energy.

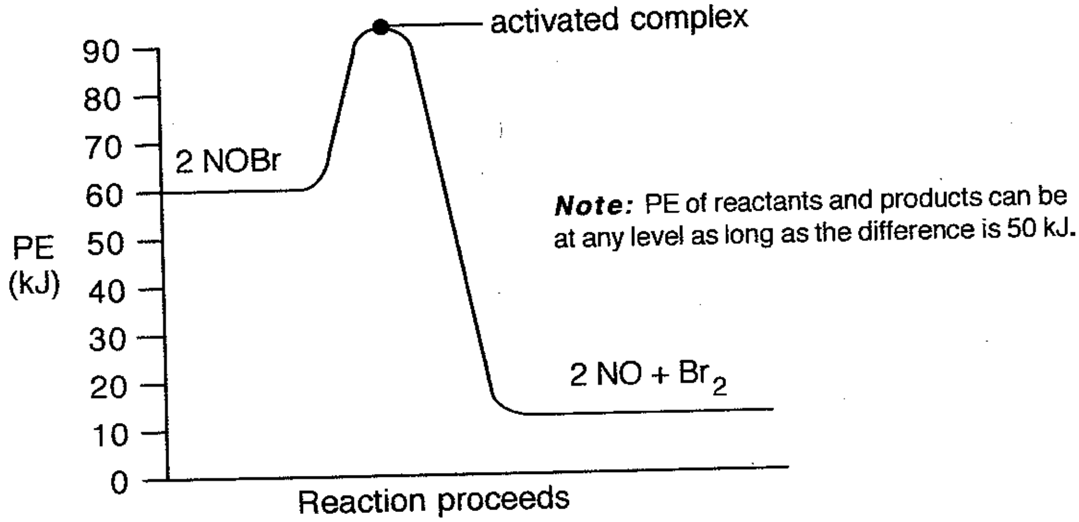
39. The reaction has a very large activation energy.

40. The kinetic energy decreases when the potential energy increases, and vice versa. Therefore, since the products have less KE then they must also possess more PE and this reaction is endothermic.

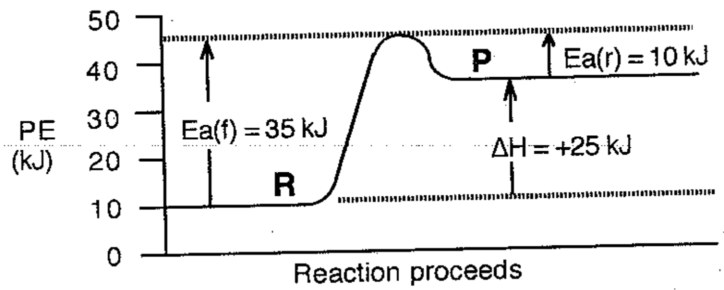
41. 55 kJ

42. endothermic ($\Delta H = +25$ kJ)

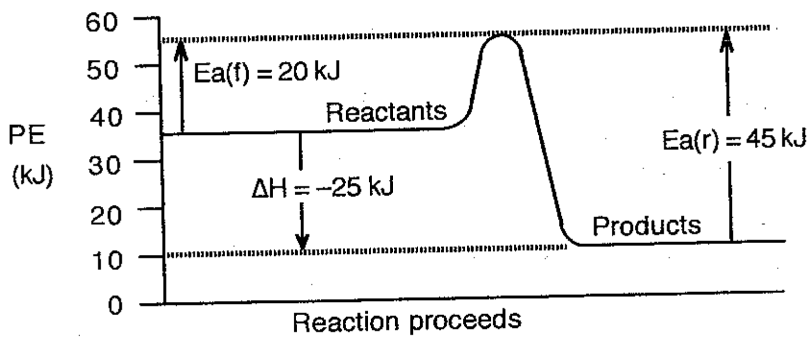
43.



44.



45.



46. (a) $2\,NO + 2\,H_2 \longrightarrow N_2 + 2\,H_2O$
(b) $[H_2O_2]$ will remain small (H_2O_2 is used up as fast as it is made)
(c) Step 1 is rate–determining
(d) NO is used in the rate–determining step and therefore the overall rate would increase.
(e) Little or no effect: speeding up a step which is not rate–determining will have little effect on the rate of the overall reaction.
(f) First step = $H_2N_2O_2$; Second step = H_4O_2 (The formulae are found by simply adding up every atom and charge found in the reactants for the step.)
(g) 2 (there are 2 steps in the mechanism)

47. An ***activated complex*** is a short–lived, unstable species which only exists after the reactants ha received an energy equal to the activation energy.

A ***reaction intermediate*** is an ordinary chemical species which is produced during one step of a reaction and used up in a subsequent step of the reaction.

48. The concentration of B would increase very quickly, and then slowly decrease as the slow second reaction steadily uses the B.

49. A reaction mechanism is the detailed sequence of actual steps in a reaction. If this reaction is a reaction mechanism, then it is a one–step reaction involving 18 molecules colliding simultaneously. Such a mechanism step is virtually impossible.

50. (a) $3\,ClO^- \longrightarrow ClO_3^- + 2\,Cl^-$ (b) reaction intermediate (c) $Cl_2O_3^{2-}$

51. (a) There are several ways to think of the process used to find the answer. Essentially, you have to see that:

FIRST EQUATION + SECOND EQUATION = OVERALL EQUATION

which rearranges to:

FIRST EQUATION = OVERALL EQUATION − SECOND EQUATION .

But, subtracting a chemical reaction equation is equivalent to interchanging the chemicals on the reactant and product sides, adding the resulting reversed equation and cancelling species which appear on opposite sides of the equations being added.

Therefore:

$$\begin{array}{lll} 2\,(CH_3)_2CO \longrightarrow & \cancel{C_2H_4} + \cancel{2\,CO} + 2\,CH_4 & \text{(overall equation)} \\ \cancel{C_2H_4} + \cancel{2\,CO} \longrightarrow & 2\,CH_2CO & \text{(add the reverse of 2nd equation)} \\ \hline 2\,(CH_3)_2CO \longrightarrow & 2\,CH_4 + 2\,CH_2CO & \text{(equals the 1st equation)} \end{array}$$

(b) First step = $C_6H_{12}O_2$; second step = $C_4H_4O_2$

52. (a)

$$\begin{array}{lll} \cancel{2\,NO} + O_2 \longrightarrow & \cancel{2\,NO_2} & \text{(overall equation)} \\ N_2O_2 \longrightarrow & \cancel{2\,NO} & \text{(add the reverse of 1st equation)} \\ \cancel{2\,NO_2} \longrightarrow & N_2O_4 & \text{(add the reverse of 3rd equation)} \\ \hline O_2 + N_2O_2 \longrightarrow & N_2O_4 & \text{(equals the 2nd equation)} \end{array}$$

(b) N_2O_4

53. (a) The Cl produced in step 3 can be used to react with another H_2 so that step 2 can occur again after step 3.
(b) The light supplies the required activation energy to break the Cl–Cl bond in Cl_2.
(c) Since the sequence of steps is: 1, 2, 3, 2, 3, 2, 3, 2, ... it appears that there is an almost endless "chain" of steps 2 & 3 linked ("chained") together.

54. Step 1 has the greatest activation energy; step 2 has the least.

55. (a) 3 steps (b) endothermic (c) endothermic

56. (a) (i) catalyst = H^+ (ii) reaction intermediate = $CH_3\text{–}CH_2^+$
(iii) overall reaction: $CH_2=CH_2 + H_2O \longrightarrow CH_3-CH_2-OH$
(b) (i) catalyst is D (ii) reaction intermediates = C and E
(iii) overall reaction: $A + 2\,B \longrightarrow 2\,F$
(c) (i) catalyst = CH_3COO^- (ii) reaction intermediates = CH_3COOH, $NHNO_2^-$ and OH^-
(iii) overall reaction: $NH_2NO_2 \longrightarrow N_2O + H_2O$

(d) (i) catalyst = Pt (ii) reaction intermediates = PtC_2H_2 and PtC_2H_4
(iii) overall reaction: $C_2H_2 + 2\,H_2 \longrightarrow C_2H_6$
(e) (i) catalyst = C (ii) reaction intermediates = B, D and G
(iii) overall reaction: $A + F \longrightarrow E + H$

57. If a catalyst is used up in one step and regenerated in a subsequent step, then obviously there is more than one step.

58. The reaction will not stop completely, but the rate of the reaction will be much less. Catalysts speed up reactions; they do not necessarily make impossible reactions occur.

59. A catalyst only decreases the activation energy; the energies of the reactants and products are not changed. Hence, ΔH can't be changed and exothermic reactions remain exothermic while endothermic reactions remain endothermic.

60. Step 1 is already very fast, so that adding a catalyst to speed it up has little or no effect on the overall reaction rate. The overall rate is controlled by the rate–determining step 3; a catalyst for this step would have a significant effect on the overall rate.

61. No change in rate. Since the original reaction mechanism has a lower activation energy, the vast majority of reacting particle will continue to take the previous, lower–energy route.

62. (a) Overall reaction: $O_3 + O \longrightarrow 2\,O_2$
(b) reaction intermediate = ClO, catalyst = Cl
(c) The chlorine atoms act as catalysts, are regenerated in the second step of the mechanism, and are available to react again. A single chlorine atom can therefore destroy large numbers of ozone molecules and only a small number of chlorine atoms need to be present in order to destroy a substantial amount of ozone.
(d) Ozone molecules absorb ultraviolet light ($h\nu$), as shown in reaction (3) of the problem statement. Since Cl atoms destroy ozone, the lowered concentration of ozone allows more ultraviolet light to reach the Earth's surface.

63. (a) Overall reaction: $CH_3OH + CH_3COOH \longrightarrow CH_3COOCH_3 + H_2O$
(b) The H^+ is consumed in the first step and regenerated in the last step.
(c) The H^+ used in the first step eventually ends up as part of a water molecule in the second step so that the water would be radioactive but the CH_3COOCH_3 would not.