

C1404.2003. ANSWER KEY with annotations

1. **SPECTROSCOPY.** In the water molecule, the total number of normal vibrational modes is....

- a) 1
- b) 2
- c) **3**
- d) 4
- e) 5

Three vibrational modes: two stretch, one bend. Using the $3n-6$ rule predicts three modes.

2. **SPECTROSCOPY.** In comparison with HCl, the frequency for the transition of DCl from the ground vibrational state to the first excited vibrational state is
- a) higher for DCl
 - b) **lower for DCl**
 - c) sometimes higher and sometimes lower, depending upon the temperature
 - d) sometimes higher and sometimes lower, depending upon the concentration
 - e) the same for both HCl and DCl

Frequency scales inversely with mass (according to Hooke's Law).

3. **SPECTROSCOPY.** To be infrared active, a diatomic molecule must be (homonuclear, heteronuclear), thereby undergoing (a net change, no net change) in dipole moment due to its vibrational motion.
- a) homonuclear, a net change
 - b) homonuclear, no net change
 - c) **heteronuclear, a net change**
 - d) heteronuclear, no net change
 - e) only triatomic molecules such as CO₂ and polyatomic molecules like hexane can be infrared active

Need a change in dipole moment.

4. **SPECTROSCOPY.** The force constant associated with vibrational modes in the infrared is associated with the stiffness of the bond and scales with multiplicity. For example, as you shift from single to double to triple bonds, the stiffness (increases, decreases) and the corresponding wave number (increases, decreases).
- a) **increases, increases**
 - b) increases, decreases
 - c) decreases, increases
 - d) decreases, decreases
 - e) force constants have nothing to do with multiplicity

Frequency scales directly with force constant (Hooke's Law)

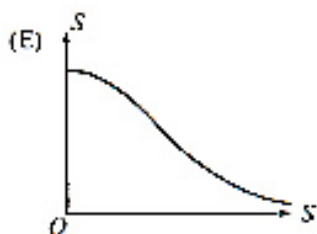
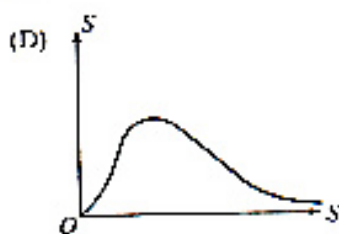
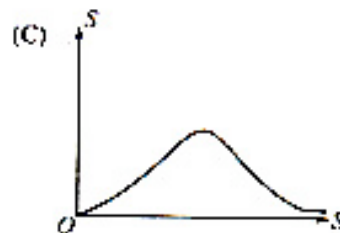
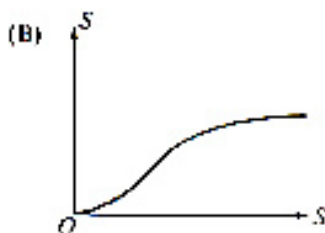
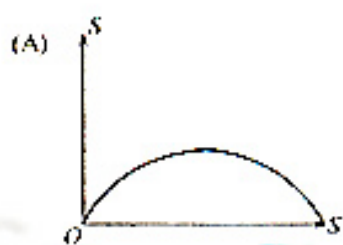
5. **SPECTROSCOPY.** Of the following molecules, the one that is not a greenhouse gas but could prove damaging to the ozone layer is

a) Methane (CH_4)
 b) Carbon tetrachloride (CCl_4)
 c) Hydrogen (H_2)
d) Chlorine (Cl_2)
 e) Ozone (O_3)

Methane, carbon tetrachloride and ozone are all greenhouse gases. Chlorine can produce atoms that initiate chain reactions, etc.

6. **GASES.** Which of the following graphs best represents the Boltzmann distribution of molecular speeds for a gas sample at a temperature of about 300K? The y-axis is the fraction of molecules with speeds designated along the x-axis:

a) A
 b) B
 c) C
d) D
 e) E



7. **GASES.** Nitrogen monoxide and oxygen are simultaneously introduced into the respective ends of a 100.0 cm length of glass tubing. At what distance from the oxygen end will there be the *first evidence* of mixing?

a) 50 cm
b) 49.2 cm
 c) 50.8 cm
 d) 40.6 cm
 e) 59.4 cm

Class problem and lecture demonstration. At same T, KE for each is the same and difference in distance traveled can be gotten from the factor 1.033, obtained from the square root of the ratio of the respective molecular weights.

8. **GASES.** In problem (7) above, what is the *first evidence* referred to?

- a) An explosion
- b) A faint white cloud
- c) **A reddish color**
- d) A flash of light
- e) Condensation of a liquid

Lecture demonstration. Oxidation of NO produces equilibrium mixture of NO₂ and N₂O₄..... and red color.

9. **GASES.** Consider gas sample A (1.00 L of He at STP) and gas sample B (2.00 L of SO₂ at 0°C and 2.00 atm and decide whether the average speed of a B molecule with respect to an A molecule is

- a) Twice as great
- b) Four times as great
- c) Half as great
- d) **One-fourth as great**
- e) The same.

Critical factor is the differences in masses and the square root of the ratio.

10. **GASES.** It is estimated that automotive air bag safety devices save about 1000 lives each year. Which one of the following most nearly represents the technology involved?

- a) Venting of liquid CO₂ as a gas from a fire extinguisher-like tank hidden under the dashboard or the side panels, inflating the air bag.
- b) Fracturing of a diaphragm, releasing tank-stored gas under pressure into the air bag.
- c) **Release on ignition of a solid-fueled, rocket-like propellant gas that inflates the air bag.**
- d) Rapid filling of the air bag with a froth of air and inert, finely divided white particulates.
- e) Expansion of a stored gas by heating as is used to inflate hot air balloons.

11. **GASES.** A CO₂ fire extinguisher works by a process most closely described by which of the following statements?

- a) Lowering the temperature of the flames to below the ignition temperature of the burning material.
- b) **Suffocating the flames as the denser CO₂ gas limits access to oxygen needed for combustion.**
- c) Spraying the liquid content of the extinguisher on the fire.
- d) Shooting particles of dry ice into the fire.
- e) Blowing out the fire by the sudden release of gas under high pressure.

12. **LIQUIDS and SOLUTIONS.** When a liquid is in equilibrium with its vapor.....
- a) the molecules still move but they no longer evaporate or condense.
 - b) the rate of evaporation is equal to the rate of condensation.**
 - c) the liquid has just completely evaporated.
 - d) all molecular motion has stopped.
 - e) You are at the triple point
13. **LIQUIDS and SOLUTIONS.** The vapor pressure of a pure liquid increases if....
- a) the surface area increases.
 - b) the number of moles increases.
 - c) the temperature increases.**
 - d) the cohesive forces increase.
 - e) the pressure increases.
14. **LIQUIDS and SOLUTIONS.** The critical conditions for carbon dioxide and ammonia are, respectively, 31.1°C and 73 atm, and 132°C and 112 atm. Therefore, at 132°C and 112 atm.....
- a) Only ammonia can be liquefied.**
 - b) Only carbon dioxide can be liquefied.
 - c) Ammonia and carbon dioxide can both be liquefied.
 - d) Neither carbon dioxide nor ammonia can be liquefied.
 - e) Ammonia and carbon dioxide only exist as aqueous ammonium hydroxide solutions or as carbonated beverages.
15. **LIQUIDS and SOLUTIONS.** Remember our little demonstration of boiling at reduced pressure? Here is a variation on that demonstration. We would like to bring to a boil a mixture of toluene and benzene of mole fraction 0.500 at a temperature of 89°C by gradually reducing the pressure on the mixture. At 89°C, p_0 for toluene is 400 torr and p_0 for benzene is 1000 torr. What is the mole fraction of the toluene in the vapor that is first condensed (distilled)?
- a) 0.267
 - b) 0.285**
 - c) 0.500
 - d) 0.937
 - e) 1.00
- Use Raoult's law to find the partial pressures of toluene and benzene, and Dalton's law for the composition of the condensed vapor:
- $$p(\text{tol}) = 400(.5) = 200; \quad p(\text{benz}) = 1000(.5) = 500; \quad p(\text{tot}) = 700$$
- $$X(\text{tol}) = 200/700 = .285$$

16. **LIQUIDS and SOLUTIONS.** In the above problem, what is the mole fraction of benzene in the vapor that is first condensed?

- a) 0.500
- b) 0.667
- c) **0.715**
- d) 0.733
- e) 0.937

$$X(\text{benz}) = 1 - X(\text{tol}) = 1 - .285 = .715$$

17. **LIQUIDS and SOLUTIONS.** A semipermeable membrane fashioned into a bag separates a 1 M solution within the bag from a 2 M solution surrounding it. The bag will...

- a) swell and the solution within will be less concentrated than 1 M.
- b) swell and the solution within will be more concentrated than 1 M.
- c) **shrivel and the solution within will be more concentrated than 1 M.**
- d) shrivel and the solution within will be less concentrated than 1 M.
- e) stay the same and the concentration won't change.

18. **LIQUIDS and SOLUTIONS.** What is the approximate freezing point of 100-proof vodka, assuming it to be a 50/50 percent-by-weight mixture of ethanol and water? Note: $K_{fp} = -1.86^\circ\text{C}/m$

- a) -2°C
- b) -4°C
- c) -20°C
- d) **-40°C**
- e) -80°C

Estimating 50/50 means about $1000\text{g}/46\text{g/mol} = 22m$ sol'n so $22(-1.86/m) = -40$

19. **LIQUIDS and SOLUTIONS.** Osmotic pressure gives large values for dilute solutions of (sparingly soluble) macromolecules such as proteins, making it an important tool for biochemists. If a particular protein is soluble to the extent of 10g/L in the vicinity of room temperature, and the osmotic pressure is 10^{-3} atm, then the MW by this method is about....

- a) 200
- b) 2000
- c) 20,000
- d) **200,000**
- e) 2,000,000

$$\pi/RT = C_{\text{mol/L}} = .001/((.082)(300)) = 4 \times 10^{-5}; \text{ sol} = 10\text{g/L}$$
$$\text{sol/conc} = 10/4 \times 10^{-5} = 200,000$$

20. **EQUILIBRIUM.** At an initial concentration of 0.100 mol/L, $\text{H}_2\text{S}(\text{g})$ and $\text{H}_2(\text{g})$ are mixed in a 1.00 L container with excess solid sulfur and allowed to come to equilibrium at 300K. For the reaction $\text{H}_2\text{S}(\text{g}) \rightleftharpoons \text{H}_2(\text{g}) + \text{S}(\text{s})$ the equilibrium constant at 300K is $K_c = 0.070$ and the reaction (as written) is endothermic. The concentration of $\text{H}_2\text{S}(\text{g})$ in mol/L at equilibrium will be.....

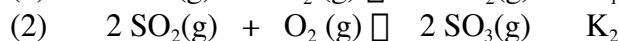
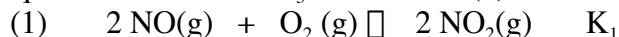
- a. 0.0131
- b. 0.0700
- c. 0.0869
- d. 0.1000
- e. **0.1869**

Equilibrium law expression : $[\text{H}_2(\text{g})]/[\text{H}_2\text{S}(\text{g})] = 1$; therefore reaction is moving left. Let x be moles H_2 reacted; $(.1 - x) = \text{moles at equilibrium}$; and $(.1 + x) = \text{moles } \text{H}_2\text{S} \text{ at equilibrium}$; then **0.1869 = mole H_2S at equilibrium.**

21. **EQUILIBRIUM.** Considering the equilibrium described in the preceding problem, adding more sulfur will (increase, decrease, leave unchanged) the total amount of $\text{H}_2\text{S}(\text{g})$ while increasing the temperature will result in an (increase, decrease, leave unchanged) the total amount of $\text{H}_2\text{S}(\text{g})$:

- a) decrease, decrease
- b) increase, increase
- c) leave unchanged, increase
- d) **leave unchanged, decrease**
- e) increase, increase

22. **EQUILIBRIUM.** Given the equilibrium constants for the following reaction, determine the equilibrium constant K_3 for reaction (3) in terms of K_1 and K_2 :



Reverse equation (1); the add (1) and (2); and take the square root to get the coefficients right. The outcome is (c):

a) $\sqrt{K_1 K_2}$

b) $\frac{K_1 K_2}{2}$

c) $\sqrt{\frac{K_2}{K_1}}$

d) $\sqrt{\frac{K_2}{2K_1}}$

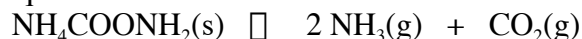
e) $\frac{K_2}{2K_1}$

23. **EQUILIBRIUM.** In a demonstration of the reaction indicated below,



equilibrium was shifted by successively reducing the room temperature mixture to ice bath, and then dry ice bath, temperatures. As a result, the intensity of the color faded, then disappeared. Consequently....

- a) the reaction must be at equilibrium at the intermediate temperature
 - b) the reaction must be complete at the lowest temperature, where the contents of the tube went colorless.
 - c) **the reaction must be exothermic**
 - d) the reaction must be endothermic
 - e) the reaction must be complete at the highest temperature, where the contents of the tube was most deeply colored.
24. **EQUILIBRIUM.** At 25°C, a sample of ammonium carbamate is decomposed into ammonia and carbon dioxide in a previously evacuated system according to chemical equilibrium that follows:



If the total pressure of the gases present is found to be 0.115 atm when the system reaches equilibrium, then the equilibrium constant K_p must be....

- a) **2.25×10^{-4}**
- b) 1.52×10^{-3}
- c) 6.08×10^{-3}
- d) 3.39×10^{-1}
- e) 3.06×10^{-1}

A third of $P(\text{tot})$ is CO_2 and two-thirds is NH_3 ; then use $K_p = p^2(\text{NH}_3)p(\text{CO}_2)$ to get (a) for the answer.

25. **SPECTROSCOPY, GASES and LIQUIDS.** Of the following, the only statement that isn't true is.....

- a) Critical temperature: $T_c = \frac{8a}{27b}$
- b) **Van der Waals gas: $(P - \frac{n^2a}{V^2})(V + nb) = nRT$**
- c) Compressibility factor for 1 mole of an ideal gas at STP: $PV/RT = 1$
- d) Energy Quanta: $\Delta E = hc\lambda$
- e) Trouton's Rule: $\Delta H/\Delta_{bp} \approx 88$