

In all questions involving gases, assume that the ideal-gas laws hold, unless the question specifically refers to the non-ideal behavior.

1. Which of the following sets of quantum numbers corresponds to one of the three highest-energy electrons in the ground state of phosphorous?

- a. $n = 4, l = 0, m_l = 0$
- b. $n = 3, l = 2, m_l = 1$
- c. $n = 4, l = 1, m_l = -1$
- d. $n = 3, l = 1, m_l = 0$
- e. $n = 5, l = 3, m_l = 2$

From the periodic table the electronic configuration of P is: $[\text{Ne}] 3s^2 3p^3$. Thus, $n = 3$ and $l = 1$ (p orbital). The value of m_l can be -1, 0, or 1. (answer d)

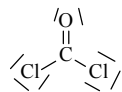
2. Which of the following molecules **does not** obey the octet rule?

- a. SiF_4
- b. PCl_5
- c. HCN
- d. CCl_4
- e. NF_3

Any atom that has more than four bonding electron pairs cannot obey the octet rule. (answer b)

3. What is the total number of lone pairs in the **best** resonance structure of COCl_2 (carbon is the central atom)?

- a. 6
- b. 7
- c. 8
- d. 9
- e. 10



The best Lewis structure (all atoms have octets) has 8 lone pairs.

4. What is the number of **unpaired** electrons in Ni?

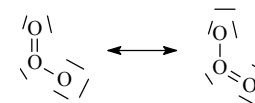
- a. 5
- b. 4
- c. 3
- d. 2
- e. 1

From the periodic table electron configuration of Ni is: $[\text{Ar}] 4s^2 3d^8$. Since there are 5 d orbitals the two d-electrons will remain unpaired (Hund's rule). (answer d)

5. Which of the following molecules has resonance structures?

- a. NH_3
- b. H_2O
- c. NF_3
- d. C_2H_6
- e. O_3

Only O_3 have double bonds, and only molecules with π bonds may need resonance structures.



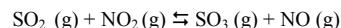
(answer e)

6. Which of the following statements is true?

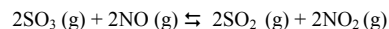
- a. Energy is required to create covalent bonds.
- b. Energy is required to break covalent bonds.
- c. Some bonds require energy to create. Others require energy to break.
- d. All C-C single bonds have exactly the same bond dissociation energies.
- e. A double bond has exactly twice the dissociation energy of the corresponding single bond.

Bonds (by definition) form because they lower the energy of the bonded species. That is energy has to be provided to break them. (answer b)

7. The value of K_c for the following reaction is 0.25.



What is the value of K_c for the reaction shown below?



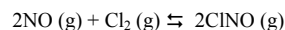
- a. 0.50
- b. 0.063
- c. 8.0
- d. 4.0
- e. 16

$$K_1 = \frac{[\text{NO}][\text{SO}_3]}{[\text{SO}_2][\text{NO}_2]}$$

$$K_2 = \frac{[\text{SO}_2]^2[\text{NO}_2]^2}{([\text{NO}]^2[\text{SO}_3]^2)} = \frac{[\text{SO}_2][\text{NO}_2]}{([\text{NO}][\text{SO}_3])^2} = (1/K_1)^2 = (1/0.25)^2 = 16$$

(answer e)

8. Consider the equilibrium:

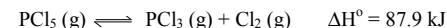


Suppose that 0.300 mol of NO, 0.200 mol of Cl_2 , and 0.500 mol of ClNO were placed in a 25.0 L vessel and allowed to reach equilibrium. At equilibrium, 0.600 mol of ClNO was present. What is the number of moles of NO present at equilibrium?

- a. 0.100 mol
- b. 0.150 mol
- c. 0.200 mol
- d. 0.250 mol
- e. 0.300 mol

The amount of ClNO increased by $(0.600 - 0.500) = 0.100$ mole. Since 2 moles of NO are needed to make two moles of ClNO, the amount of NO would decrease by 0.100 mole. The number of moles of NO remaining at equilibrium will be $(0.300 - 0.100) = 0.200$ (answer c)

9. For the following reaction at equilibrium, which of the listed perturbations will cause an **increase** in the equilibrium concentration of the reactant?

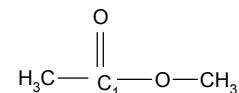


- a. Chlorine gas is removed from the reaction vessel.
- b. The temperature of the reaction vessel is increased.
- c. The volume of the reaction vessel is decreased.
- d. Ar (g) is added to the reaction vessel.
- e. The pressure of the system is decreased.

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- a) If the chlorine is removed, the equilibrium concentration of PCl_5 will decrease.
 - b) Since the reaction is endothermic, increasing temperature will increase products at the expense of PCl_5 .
 - c) If the volume is decreased, the pressure will increase. To lower the pressure the system will shift to the left (one mole of reagents gives two moles of products). The concentration of PCl_5 will increase.
 - d) Inert gas does not affect the equilibrium concentrations.
 - e) If the pressure is decreased, the system will shift to the right, to increase the pressure (there are two moles of product, but only one mole of reactant).

(answer c)

10. What is the hybridization of C_1 and the O-C-O bond angle in the following molecule?



Note: Lone pairs and the molecular geometry are **not** shown explicitly in this structure.

- a. sp^3 120°
- b. sp_2 180°
- c. sp^2 120°
- d. sp_3 109.5°
- e. sp^2 109.5°

C_1 forms one π bond, and three σ bonds. It is, therefore sp^2 , hybridized (one p orbital set aside for the π system). Three electron domains are 120° apart to minimize repulsions. (answer c)

11. What is the **molecular** geometry of ClF_3 ?

- a. T-shaped
- b. trigonal planar
- c. trigonal bipyramidal
- d. trigonal pyramidal
- e. seesaw

In ClF_3 there are 3 bonding pairs and two non-bonding electron pairs. The electron domain structure is trigonal bipyramid. The lone pairs (to be as far from each other as possible) will be in the equatorial plane (120° apart). Thus the molecular structure will be T-shaped (90° bond angles). (answer a)

12. Which one of the following molecules is **nonpolar**?

- a. XeF_4
- b. SF_4
- c. NO_2^-
- d. NH_3
- e. BrF_5

a) Xe has four bonding pairs and two lone-pairs: octahedral electronic structure, with lone pairs in axial positions (planar molecular structure). Bond dipoles cancel.
b) S has four bonding pairs and one lone pair: trigonal bipyramidal electronic structure, with the lone pair in the equatorial position (seesaw molecular structure). The bond dipoles do not cancel.
c) N has three bonding pairs (one π) and one lone pair. The electronic structure is trigonal planar with one lone pair (resonance structures are present, the molecular structure is bent). The bond dipoles do not cancel.
d) N has three bonding pairs and one lone pair. The electronic structure is tetrahedral. The molecular structure is trigonal pyramidal. The bond dipoles do not cancel.
e) Br has five bonding pairs, and one lone pair. The electronic structure is octahedral, and the molecular structure is square pyramidal. The bond dipoles do not cancel.

(answer a)

13. Glycerin ($\text{C}_3\text{H}_8\text{O}_3$) is a nonvolatile nonelectrolyte. What is the vapor pressure at 25°C of a solution made by adding 9 mol of glycerin to 270.0 mL of water? (assume the vapor pressure of pure water at 25°C is 23.8 torr, and the density of water is 1 g/mL)

- a. 793 torr
- b. 0.768 torr
- c. 0.793 torr
- d. 23.8 torr
- e. 14.9 torr

$P_A = X_A P_A^0$; Moles of water $270/18 = 15$ moles, $X_{\text{H}_2\text{O}} = 15/(15 + 9) = 0.625$

$P_{\text{H}_2\text{O}} = 0.625 (23.8) = 14.88$ torr (answer e)

14. Consider the following three balanced chemical reactions run under conditions of a constant temperature (28°C) and a constant volume (1 L). Which reaction **would not** result in a change in pressure?

- I. $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$
- II. $2\text{NH}_3(\text{g}) \rightarrow 2\text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$
- III. $\text{NH}_4\text{NO}_2(\text{s}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$

- a. I only
- b. II only
- c. III only
- d. I and II only
- e. I, II, and III

Only reaction I has the same number of moles of gas molecules on both sides of the equation. Such reactions do not lead to change in pressure. (answer a)

15. The volume of a large, irregularly shaped tank is determined as follows. The tank is first evacuated, and then it is connected to a 50.0 L cylinder of compressed helium gas. The gas pressure in the cylinder, originally at 21 atm, falls to 7 atm without a change in temperature. What is the volume of the tank?

- a. 100 L
- b. 200 L
- c. 300 L
- d. 400 L
- e. 500 L

$P_1 V_1 = P_2 (V_1 + V_2)$ $V_2 = (P_1 V_1 / P_2) - V_1 = (21 \cdot 50 / 7) - 50 = 100$ L (answer a)

16. The density of an unknown gas is 1.25 g/L at STP. Which of the following is most likely to be the unknown gas?

- a. CO
- b. O_2
- c. C_2H_6
- d. NH_3
- e. Cl_2

$d = PM/RT$ or $M = dRT/P = 1.25 \cdot 0.08206 \cdot 273 / 1 = 28.00$ g/mol, which corresponds to the molecular weight of CO. (answer a)

17. A 3.0 L sample of He gas at 6 atm and 25 °C, and a 4.5 L sample of Ne gas at 2.0 atm and 25 °C are completely transferred to a 9.0 L flask, at constant temperature. What is the total pressure in the 9.0 L flask?

- 1.0 atm
- 2.0 atm
- 3.0 atm
- 4.0 atm
- 5.0 atm

PV = nRT: for He: $n_1 = P_1V_1/RT$, for Ne $n_2 = P_2V_2/RT$; for both gases $P_fV_f = (n_1 + n_2)RT$, where T is constant. Thus, $P_f = [(P_1V_1/RT + P_2V_2/RT)RT]/V_f$ or:
 $P_f = (P_1V_1 + P_2V_2)/V_f = (3 \cdot 6 + 2 \cdot 4.5)/9 = 3$ atm (answer c)

18. Caffeine has a molecular weight of 194.2 g/mol and mass composition of 49.98% C, 5.19% H, 28.25% N, and 16.48% O. What is the **molecular formula** of caffeine?

- $C_{10}H_{14}N_2O_2$
- $C_8H_{10}N_4O_2$
- $C_8H_{10}N_2O$
- $C_4H_5N_2O$
- C_5H_7NO

Shortcut solution: only (a) and (b) have MW = 194 g/mol. Answers (d) and (e) can be excluded without calculations (too small). MW of (c) = 150 g/mol. The N to O ratio can be obtained from the percent of N and O. For N: 28.25/14; for O: 16.48/16. This clearly indicates answer b (2:1 ratio) (answer b)

Full work (not really necessary):

$$C: 49.98/12 = 4.165$$

$$H: 5.19/1 = 5.19$$

$$N: 28.25/14 = 2.02$$

$$O: 16.48/16 = 1.03$$

The ratio of C:H:N:O is 4:5:2:1. Of the choices available (d) or (b) only (b) has correct MW

19. Which of the following liquids has extensive hydrogen bonding?

- CH_4
- H_2NNH_2
- CH_3F
- $H_3C-O-CH_3$
- CH_2Cl_2

Only (b) has an electronegative atoms with lone pairs (N) and hydrogens attached to electronegative atoms (N-H). (answer b)

20. List the following substances in order of **increasing** normal boiling points.

$BaCl_2$, CO, HF, Ne

- $CO < HF < Ne < BaCl_2$
- $HF < CO < BaCl_2 < Ne$
- $Ne < CO < HF < BaCl_2$
- $BaCl_2 < HF < CO < Ne$
- $Ne < CO < BaCl_2 < HF$

All molecules have dispersive interactions, but also:

$BaCl_2$ is an ionic substance (solid at STP) with strong intermolecular interactions (ion-ion).

CO is a polar substance (gas at STP) with weak dipole-dipole interactions.

HF is a polar substance (liquid at STP) with strong hydrogen bonding.

Ne is nonpolar substance (gas at STP) with weak London dispersive interactions only.

The boiling point will be the lowest for the weakest interactions. (answer c)

21. Which of the following aqueous solutions will show the largest freezing point depression?

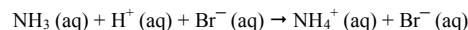
- 0.01 M HCl
- 0.03 M $CaBr_2$
- 0.02 M $Ca(NO_3)_2$
- 0.02 M $Al(NO_3)_3$
- 0.02 M $Al_2(SO_4)_3$

The freezing-point depression depends on the number of particles in solution. The largest concentration of particles is in $Al_2(SO_4)_3$ ($0.02 \times 5 = 0.1$ M). (answer e)

22. Which of the following represents the net ionic equation for the reaction of NH_3 (aq) and HBr (aq)?

- $NH_3(aq) + HBr(aq) \rightarrow NH_4^+(aq) + Br^-(aq)$
- $HBr(aq) \rightarrow NH_4Br(aq)$
- $NH_3(aq) + H^+(aq) + Br^-(aq) \rightarrow NH_4Br(aq)$
- $NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$
- $N^{3-}(aq) + 3H^+(aq) + H^+(aq) + Br^-(aq) \rightarrow NH_4Br(aq)$

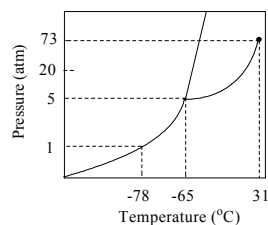
It is an acid-base reaction (d) with NH_3 as the base:



Ammonia does not dissociate in water to a significant degree, and Br^- is the spectator ion (is on both sides of the equation) and does not participate in the "net" reaction. (answer d)

23. According to the phase diagram below, what phase transition(s) will take place when CO₂ is heated from -70 °C to 31 °C at a constant pressure of 20 atm?

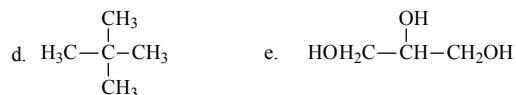
- deposition
- condensation, then freezing
- melting, then vaporization
- sublimation
- vaporization



At -70 °C and 20 atm CO₂ is a solid, it melts at ca. -55 °C at this pressure, and then evaporates to a gas at ca. 20 °C at this pressure. The line drawn at 20 atm crosses two phase-transition lines between -70 and 31 °C. (answer c)

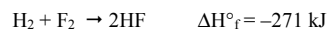
24. Which of the following compounds has the highest vapor pressure at 0 °C?

- H₃C—(CH₂)₃—CH₃
- H₃C—(CH₂)₂—CH₂OH
- HOH₂C—CH₂—CH₂OH



Although all molecules have similar sizes (and therefore similar dispersive forces), (b), (c) and (e) are hydrogen-bonded (liquids), and thus have lower vapor pressure than (a) or (d) which have dispersive interactions only. Of the two pentanes, (a) and (d) one with larger surface area (a) will have more dispersive interactions (more points of "contacts" between molecules possible). Thus (d) will be most volatile (highest vapor pressure). (answer d)

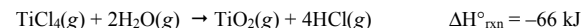
25. How many grams of F₂ need to be consumed to produce 338 kJ of heat in the following reaction?



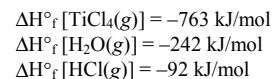
- 15.2 g
- 47.4 g
- 23.7 g
- 30.5 g
- 11.8 g

Consumption of one mole of F₂ produces 271 kJ of heat. To produce 338 kJ one need to use (338/271) = 1.247 mole. MW of F₂ is 38 g/mol; thus 1.247 mole is 47.4 g. (answer b)

26. Titanium (IV) oxide, one of the most commonly used white paint pigments, is produced by the following reaction:



Given the following ΔH°_f , what is ΔH°_f for TiO₂(g)?



- 813 kJ/mol
- 32 kJ/mol
- 945 kJ/mol
- 1129 kJ/mol
- 979 kJ/mol

$$\Delta H^\circ_{\text{rxn}} = \sum n \Delta H^\circ_f(\text{products}) - \sum m \Delta H^\circ_f(\text{reactants})$$

$$-66 = [\Delta H^\circ_f(\text{TiO}_2) + 4(-92)] - [(-763) + 2(-242)] \text{ from where:}$$

$$\Delta H^\circ_f(\text{TiO}_2) = -66 + (-763 - 484) + 368 = -945 \text{ kJ} \quad (\text{answer c})$$

27. Which of the following atoms has the smallest ionization energy?

- Ne
- O
- N
- Ar
- Na

Ionization energy is the lowest for metals. Na is the only metal listed. By losing one electron it achieves the noble-gas electronic configuration. (answer e)

28. Which of the following orderings of atomic/ionic radii is correct?

- Li < Li⁺ < He
- N < O < F
- Br < Cl < F
- Li < Na < K
- Mg < Mg⁺ < Mg²⁺

In general, the size (radius) decreases from left to right in the same row (effective charge), and by removing electrons (forming cations). In general the size increases going down a column. Thus only (d) can be correct. (answer d)

29. Which of the following would be expected to have the lowest melting point?

- a. NaCl
- b. MgO
- c. MgS
- d. NaBr
- e. LiCl

They are all ionic solids. The one with the smallest ion charges, and the largest ion-ion distances will have the smallest lattice energy and the lowest melting point. NaBr has mono-charged ions, and the Na and Br are the largest ions between all the non-charged salts. (answer d)

30. At 20 °C, Henry's law constant for Ar is half of that for Kr. If a gaseous Ar/Kr mixture containing 20% molar fraction of Kr is placed over water at 20 °C, what is the **ratio** of concentrations of Ar to Kr in water?

- a. 0.5
- b. 1.0
- c. 2.0
- d. 3.0
- e. 4.0

$C_g = kP_g$ for Ar: $C_1 = k_1P_1$, for Kr: $C_2 = k_2P_2$.

Thus, $C_1/C_2 = (k_1/k_2) (P_1/P_2)$.

For gases the partial pressures are proportional to the molar fractions, i.e. $(P_1/P_2) = 80/20$ and:

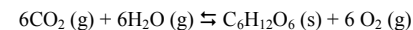
$C_1/C_2 = (k_1/k_2) (P_1/P_2) = 0.5 (80/20) = 2.0$ (answer c)

31. Which of the following would be expected to be most soluble in H₂O?

- a. ethanol
- b. benzene
- c. butane
- d. bromine
- e. trichloromethane

Only ethanol, CH₃CH₂OH, is capable of forming hydrogen bonds with water (both donate and accept such bonds). Like dissolves like. (answer a)

32. What is the correct expression for the equilibrium constant for the following reaction?



- a. $K_c = \frac{[\text{O}_2]^6}{[\text{CO}_2]^6}$
- b. $K_c = \frac{[\text{CO}_2]^6}{[\text{O}_2]^6}$
- c. $K_c = \frac{[\text{C}_6\text{H}_{12}\text{O}_6][\text{O}_2]^6}{[\text{CO}_2]^6[\text{H}_2\text{O}]^6}$
- d. $K_c = \frac{[\text{CO}_2]^6[\text{H}_2\text{O}]^6}{[\text{C}_6\text{H}_{12}\text{O}_6][\text{O}_2]^6}$
- e. $K_c = \frac{[\text{O}_2]^6}{[\text{CO}_2]^6[\text{H}_2\text{O}]^6}$

The K_c expression must have the product concentrations in the numerator (to the appropriate power; 6 for O₂, and should not include pure solids (or liquids); i.e. [C₆H₁₂O₆] is constant and incorporated into the K_c value) and reagent concentrations (to the 6-power in this case) in the denominator. (answer e)

33. Which of the following statements correctly describes all systems **at equilibrium**?

- I. The rate of the forward reaction is equal to the rate of the reverse reaction.
- II. The concentrations of the reactants and products remain constant.
- III. Concentrations of products are equal to the concentrations of the reactants.
- IV. The heat of formation of the products equals the heat of formation of the reactants.

- a. III only
- b. I and II, only
- c. II and III, only
- d. III and IV, only
- e. IV only

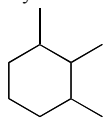
I is true.

II is true.

III is not generally true (it could be so in some specific cases).

IV is not generally true (it could be so in some specific cases). (answer b)

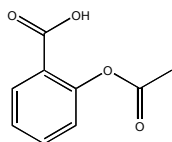
34. What is the correct systematic (IUPAC) name for the following molecule?



- a. 1, 2, 3- trimethylbenzene
- b. 1, 2, 3- trimethylhexane
- c. 1, 2, 3- trimethylcyclononane
- d. 1, 2, 3- trimethylcyclohexane
- e. 1, 2, 3- trimethylcycloheptane

It is a cyclic alkane (cyclohexane) with three methyl groups on carbons 1,2,3. (answer d)

35. Which two functional groups are present in aspirin?

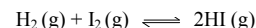


aspirin

- a. aldehyde and amide
- b. carboxylic acid and ester
- c. carboxylic acid and ether
- d. alcohol and ester
- e. ketone and aldehyde

-COOH at the top is a carboxylic acid, R-O-C(O)CH₃ is an ester (of acetic acid). (answer b)

36. Consider the following reaction at a constant temperature for which $K_p = 7.0$:



Hydrogen (H_2 , 0.150 moles), I_2 (0.500 moles), and HI (0.600 moles) are introduced into a 2.0 L vessel. Which one of the following statements is true at the moment of mixing?

- a. The system is at equilibrium.
- b. The system is at equilibrium, but adding a catalyst will cause the reaction to proceed to the right.
- c. The system is not at equilibrium, and will proceed to the left to achieve equilibrium.
- d. The system is not at equilibrium, and will proceed to the right to achieve equilibrium.
- e. The system is not at equilibrium, and it cannot achieve equilibrium.

For this reaction $K_p = K_c$ (the same number of moles on the left and right), and with a constant volume: $Q = (0.6)^2 / [(0.15)(0.5)] = 4.8 < K_c$. To reach equilibrium the product should increase, and the reactants should decrease, i.e. the system will shift to the right. (answer d)

37. What is the osmotic pressure of a 0.100 M solution of a nonelectrolyte at 20 °C?

- a. 1.00 atm
- b. 2.41 atm
- c. 0.164 atm
- d. 4.82 atm
- e. 1.64 atm

$\pi = (n/V)RT$, $\pi = 0.1 \cdot 0.0821 \cdot (273+20) = 2.41$ atm (answer b)

38. Which species is **primarily** responsible for absorbing ultraviolet radiation in the atmosphere?

- a. H_2O
- b. N_2
- c. CO_2
- d. CCl_2F_2
- e. O_3

Ozone with its π system is most efficient in absorbing UV radiation, especially that around 300 nm. (answer e)

39. Which of the following processes is endothermic?

- a. $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$
- b. $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$
- c. $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
- d. $\text{CO}_2(\text{g}) \rightarrow \text{CO}_2(\text{s})$
- e. $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$

All combustions are exothermic: (a), (c). All processes decreasing kinetic energy of molecules are exothermic: (b), (d). Only vaporization (increasing kinetic energy) is endothermic (answer e)

End of the exam