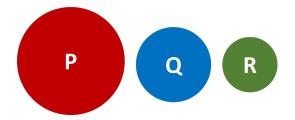


SECTION I

1. Illustrated below are the atomic sizes of three different elements from the same period. Which of the following statements is true?



(A) The first ionization energy will be greatest in element P.

(B) The effective nuclear charge would be greatest in element P.

(C) The electronegativity will be greatest in element R.

(D) The electron shielding effect will be greatest in element R.

2. Arrange the following atoms in order of increasing first ionization energy, IE_1 .

Ge	As	Р
Germanium	Arsenic	Phosphorus

(A) P < Ge < As

(B) P < As < Ge

(C) As < Ge < P

(D) Ge < As < P

3. According to VSEPR theory, the geometry (with lone pair) around the central iodine in the ions I_3^+ and I_3^- are, respectively:

- (A) Tetrahedral in both cases.
- (B) Trigonal bipyramidal in both cases.
- (C) Tetrahedral and trigonal bipyramidal.
- (D) Tetrahedral and octahedral.

4. The shape of the [SF₂Cl] ⁺ ion relatively to the central sulfur atom is

- (A) Trigonal planar.
- (B) Tetrahedral.
- (C) Trigonal pyramidal.
- (D) See saw.

5. The following set of kinetics data was obtained for the reaction

$$S_2O_8^{2-}(aq) + 3I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_3^-(aq)$$

[S ₂ O ₈ ^{2–}], M	[I ⁻], M	Initial rate, $M \cdot sec^{-1}$
0.25	0.10	9.0×10 ⁻³
0.10	0.10	3.6×10 ⁻³
0.20	0.30	2.16×10 ⁻²

What is the rate law for this reaction?

(A) Rate = $k[S_2O_8^{2-}][I^-]$ (B) Rate = $k[S_2O_8^{2-}]^2[I^-]$ (C) Rate = $k[S_2O_8^{2-}][I^-]^2$ (D) Rate = $k[S_2O_8^{2-}][I^-]^3$ **6.** The standard heat of formation of HF(g) is -270 kJ. The bond dissociation energies of H-H and H-F are 440 kJ and 565 kJ, respectively. Using these data, what is the bond dissociation energy of a F-F bond?

- **(A)** 98 kJ
- **(B)** 150 kJ
- (C) 189 kJ
- **(D)** 212 kJ

7. The number of moles of metallic zinc necessary to produce 224 mL of hydrogen gas at STP by reaction with a strong acid is:

- **(A)** 0.001 mol
- **(B)** 0.002 mol
- **(C)** 0.01 mol
- **(D)** 0.02 mol

8. The partial pressure-based equilibrium constant K_p equals the concentration-based equilibrium constant K_c for which of the following equilibria?

(A)
$$H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(\ell)$$

(B) $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$
(C) $2 CH_4(g) + 3O_2(g) \rightleftharpoons 2CO(g) + 4H_2O(g)$
(D) $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$

9. Consider the reaction

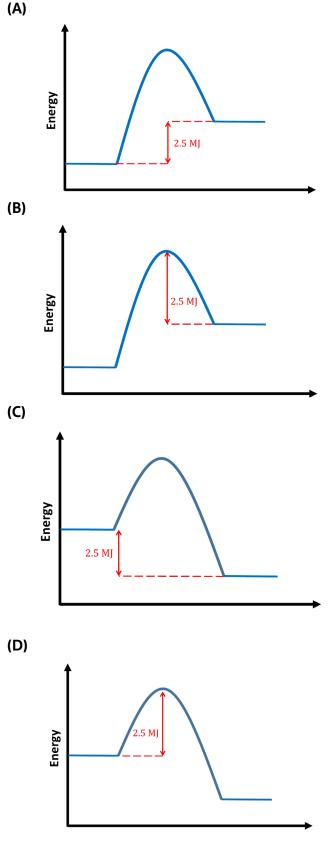
 $2 \operatorname{NO}(g) \rightleftharpoons \operatorname{N}_2(g) + \operatorname{O}_2(g)$

If the initial partial pressure of NO(g) is 1.0 bar, and x is the equilibrium concentration of N₂(g), what is the correct equilibrium relation?

(A) $K = \frac{2x}{(1.0-x)^2}$ (B) $K = \frac{x^2}{(1.0-2x)}$ (C) $K = \frac{x^2}{(1.0-2x)^2}$ (D) $K = \frac{4x^3}{(1.0-2x)^2}$ **10.** Burning of acetylene has a standard enthalpy of combustion of about -2.5 MJ.

$$2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(\ell)$$

Which of the following energy diagrams correctly describes this reaction?



11. Which of the following processes is accompanied by a decrease in entropy?

(A) Dissolution of urea in water.

(B) Isothermal compression of an ideal gas.

(C) Fusion of a solid at atmospheric pressure.

(D) Heating of a liquid from 298 K to its boiling point at constant pressure.

12. The molar solubility of a sparingly used soluble salt MX_4 is S. The corresponding solubility product is K_{sp} . What is the value of S in terms of K_{sp} ? **(A)** $S = (K_{sp}/128)^{1/4}$ **(B)** $S = (256K_{sp})^{1/4}$ **(C)** $S = (K_{sp}/256)^{1/5}$ **(D)** $S = (128K_{sp})^{1/5}$

13. The solubility product of Mg(OH)₂ is 1.0×10^{-11} . What minimum pH must be attained to decrease the concentration of Mg²⁺ ions in a solution of Mg(NO₃)₂ to less than 10^{-7} M?

(A) 10

(B) 11

(C) 12

(D) 13

SECTION II

Problem 1

The pressure-based equilibrium constant K_p for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

is 49 at 460°C. Suppose we introduce H_2 and I_2 in a closed flask, each at an initial pressure of 0.5 atm.

A. Is this equilibrium homogeneous or heterogeneous? Why? (10%)

B. Determine the partial pressures of each gas at equilibrium. (30%)

Species	Equilibrium
	pressure
H ₂	
I ₂	
HI	

C. Determine the equilibrium constant based on molar concentrations, K_c . (10%) The rate constant for the decomposition of HI on a gold surface is 0.08 M·s⁻¹.

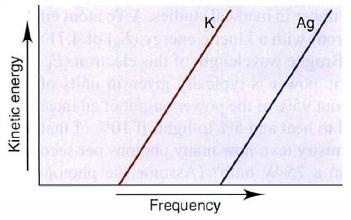
$$2\mathrm{HI}(g) \rightarrow \mathrm{H}_{2}(g) + \mathrm{I}_{2}(g)$$

D. What is the order of the reaction? (25%)

E. How long will it take for the concentration of HI to drop from 2.0 M to 0.75 M? (25%)

Problem 2

The photoelectric effect is illustrated in a plot of the kinetic energies of electrons ejected from the surface of potassium metal or silver metal at different frequencies of incident light.



- A. Why don't the lines begin at the origin? (25%)
- **B.** Why don't the lines begin at the same point? (25%)
- C. From which metal will light of a shorter wavelength eject an electron? (25%)
- D. Why are the slopes of the lines equal? (25%)



\rightarrow Section I

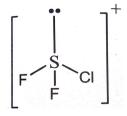
1.C. As we progress across a period, the number of protons increases and the attraction of electrons to the nucleus intensifies accordingly. Thus, one can surmise that atom R has the highest electronegativity.

2.D. IE_1 decreases down a group, so arsenic will have a lower IE_1 than phosphorus. (One simplistic way to explain this trend is to recall that atomic size increases as we move down a group, so the outermost electrons of a large atom such as, say, arsenic will experience a milder electrostatic attraction to the nucleus than the external electrons of a smaller atom such as phosphorus.) According to the "period rule," ionization energy increases across a period, that is, as elements increase their number of protons. This implies that As has a higher IE_1 than Ge.

3.C. The geometry (with lone pair) around the central iodine in I_3^+ and I_3^- ions are tetrahedral and trigonal bipyramidal, respectively.

lon	No. lone pairs + bond pairs	Geometry	Shape
I_{3}^{+}	2 LP + 2 BP	Based on tetrahedral	Angular (bent shape)
I_3^-	3 LP + 2 BP	Based on trigonal bipyramidal	Linear

4.C. $[SF_2Cl]^+$ ion has a central sulfur atom with one lone pair of electrons and sp^3 hybridization; accordingly, it has a trigonal pyramidal shape.



5.A. One can solve these concentration-reaction rate problems with little recourse to calculations. Notice that from the second row to the first, the concentration of peroxydisulfate ion is multiplied by 2.5 and the initial rate is likewise increased 2.5-fold; accordingly, we can surmise that the reaction is first order with respect to $S_2O_8^{2-}$. In the transition from the second row to the third, the concentration of $S_2O_8^{2-}$ is doubled, the concentration of I⁻ is tripled, and the initial rate increases six-fold. Since we already know that doubling the concentration of $S_2O_8^{2-}$ will double the reaction-rate, the remainder of the six-fold rate increase must've come from the increased concentration of iodide ion. Accordingly, the reaction is also first order relatively to I⁻. The reaction rate is ultimately given by

$$\operatorname{Rate} = k \left[\operatorname{S}_{2} \operatorname{O}_{8}^{2^{-}} \right] \left[\operatorname{I}^{-} \right]$$

6.B. The pertaining reaction is the formation of hydrogen fluoride from gaseous hydrogen and fluorine,

$$\frac{1}{2}\mathrm{H}_{2}(g) + \frac{1}{2}\mathrm{F}_{2}(g) \to \mathrm{HF}(g)$$

which has a heat of reaction equal to -270 kJ. Equipped with this enthalpy and the bond energies we were given, the bond energy we aim for is

$$-270 = \frac{1}{2} \times 440 + \frac{1}{2} \times H_{F-F} - 565$$

$$\therefore -270 = 220 + \frac{1}{2} \times H_{F-F} - 565$$

$$\therefore -270 = \frac{1}{2} \times H_{F-F} - 345$$

$$\therefore H_{F-F} = 150 \text{ kJ}$$

7.C. Zinc is corroded by a strong acid such as HCl to yield a salt and gaseous hydrogen,

$$\operatorname{Zn}(s) + 2\operatorname{HCl}(\ell) \rightarrow \operatorname{ZnCl}_2(s) + \operatorname{H}_2(g)$$

Clearly, one mole of zinc produces one mole of hydrogen gas and, since the molar volume at STP is 22.4 L/mol, we can state that

$$\frac{1 \mod Zn}{22.4 \text{ L H}_2} = \frac{x}{224 \times 10^{-3} \text{ L H}_2}$$
$$\therefore x = \frac{224 \times 10^{-3}}{22.4} = \boxed{0.01 \mod Zn}$$

8.B. Noting that $K_p = K_c(RT)^{\Delta n}$, the two equilibrium constants will have the same value if $\Delta n = 0$, that is, if the number of equivalents of gas is the same on both sides of the reaction. Such is the case of reac tion (B), where we have two equivalents of gas on the side of the reactants and two equivalents of gas on the side of the products.

9.C. Set up an equilibrium table.

	2 NO(<i>g</i>)	\leftrightarrow	$N_2(g)$	$O_2(g)$
Initial composition	1.0	\leftrightarrow	0	0
Change in comp.	-2x	\leftrightarrow	x	x
Final comp.	1.0 - 2x	\leftrightarrow	x	x

Next, appealing to the law of mass action, we get

$$K_{eq} = \frac{[N_2][O_2]}{[NO]^2} = \frac{x \times x}{(1.0 - 2x)^2} = \frac{x^2}{(1.0 - 2x)^2}$$

10.C. The reaction is endothermic, so the energy level of products is lower than the energy level of reactants; this excludes alternatives (A) and (B). The reaction enthalpy is the difference in energy level of products and reactants, as illustrated in (C). The energy range indicated in (D) is actually the activation energy of the reaction.

11.B. In isothermal compression, the change in entropy is given by the usual equation

$$\Delta S = \frac{Q}{T}$$

Since $\Delta U = 0$, the first law yields

$$Q = \Delta U + W \to Q = W$$

and, of course, $W = P\Delta V$. Substituting in the equation for ΔS brings to

$$\Delta S = \frac{Q}{T} = \frac{W}{T} \to \Delta S = \frac{P\Delta V}{T}$$

Since we are considering a compression, $\Delta V < 0$ and, accordingly, $\Delta S < 0$. It is intuitive that compressing a gas with no change in temperature decreases its level of disorder.

12.C. We begin by di	rawing up a con	centration table.
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	MX ₄	\leftrightarrow	M ⁴⁺	4 X ⁻
Initial	—	\leftrightarrow	0	0
Reaction	—	\leftrightarrow	+S	+4S
Final	—	\leftrightarrow	S	4 <i>S</i>

Then, appealing to the law of mass action, a relationship between S and K_{sp} can be established,

$$K_{sp} = \left[\mathbf{M}^{4+} \right] \left[\mathbf{X}^{-} \right]^{4}$$
$$\therefore K_{sp} = S \times (4S)^{4} = 256S^{5}$$
$$\boxed{S = \left(K_{sp} / 256 \right)^{1/5}}$$

13.B. The solubility product expression for magnesium hydroxide is

$$K_{sp} = \left[\mathrm{Mg}^{2+}\right] \left[\mathrm{OH}^{-}\right]^{2} = 1.0 \times 10^{-11}$$

Substituting $[Mg^{2+}]$ = $10^{\text{-7}}$ M and solving for the concentration of hydroxyl, we get

$$\begin{bmatrix} Mg^{2+} \end{bmatrix} \begin{bmatrix} OH^{-} \end{bmatrix}^{2} = 1.0 \times 10^{-11} \rightarrow 10^{-7} \times \begin{bmatrix} OH^{-} \end{bmatrix}^{2} = 10^{-11}$$
$$\therefore \begin{bmatrix} OH^{-} \end{bmatrix}^{2} = \frac{10^{-11}}{10^{-7}} = 10^{-4}$$
$$\therefore \begin{bmatrix} OH^{-} \end{bmatrix} = 10^{-2} M$$

so that pOH = 2 and pH = 14 - 2 = 12.

Answer Summary			
1	U	8	В
2	D	9	С
3	С	10	С
4	С	11	В
5	Α	12	С
6	В	13	В
7	C		

ightarrow Section II

Problem 1

(A) The equilibrium is homogeneous because all reactants and products are in the same (gaseous) phase.

(B) First, we draw up a concentration table.

	H ₂	I ₂	\leftrightarrow	2 HI
Initial	0.5	0.5	\leftrightarrow	0
Reaction	-X	-X	\leftrightarrow	+2 <i>X</i>
Final	0.5 <i>-X</i>	0.5 <i>-X</i>	\leftrightarrow	2 <i>X</i>

Then, we write the law of mass action,

$$\frac{\left[\mathrm{HI}\right]^{2}}{\left[\mathrm{H}_{2}\right]\left[\mathrm{I}_{2}\right]} = 49$$
$$\therefore \frac{\left(2X\right)^{2}}{\left(0.5 - X\right)\left(0.5 - X\right)} = 49$$
$$\therefore \left(\frac{2X}{0.5 - X}\right)^{2} = 49$$
$$\therefore \frac{2X}{0.5 - X} = 7$$
$$\therefore 2X = 3.5 - 7X$$
$$\therefore X = \frac{3.5}{9} = 0.389 \text{ atm}$$

Thus, the equilibrium concentrations are

$[H_2] = [I_2] = 0.5 -$	0.389 = 0.111 atm
$[\mathrm{HI}] = 2X = 2 \times 0$.389 = 0.778 atm
Spacias	Equilibrium

Species	Equilibrium
	concentration
H ₂	0.11 atm

I ₂	0.11 atm
HI	0.78 atm

(C) The pressure-based equilibrium constant K_p is related to the concentration-based constant K_c by the simple expression

$$K_p = K_c \left(RT \right)^{\Delta n}$$

where Δn is the variation in the number of moles of gas from reactants to products. Notice that in the reaction at hand the number of equivalents of gas is 2 on both sides of the reaction; as a result, $\Delta n = 2$ -2 = 0 and the concentration-based equilibrium constant turns out to have the same value as K_p ,

$$K_p = K_c (RT)^{\Delta n} \to K_c = \frac{K_p}{(RT)^{\Delta n}}$$
$$\therefore K_c = \frac{49}{(0.0821 \times 733)^0} = \boxed{49}$$

(D) Since the rate constant has units of M/sec, the reaction is zeroth order in nature.

(E) For a zeroth-order reaction, the concentration of reactant varies with time following the linear function

$$\left[\mathrm{HI}\right]_{0} - \left[\mathrm{HI}\right] = akt$$

where $[HI]_0 = 2.0 \text{ M}$, [HI] = 0.75 M, a = 2 is the stoichiometric coefficient that accompanies HI, and $k = 0.08 \text{ M} \cdot \text{s}^{-1}$; thus,

2.0 − 0.75 = 2×0.08×t

$$\therefore t = \frac{1.25}{0.16} = \boxed{7.81 \text{ s}}$$

Problem 2

(A) The lines do not begin at the origin because an electron must absorb a minimum amount of energy before it has enough energy to overcome the attraction of the nucleus and leave the atom. This minimum energy is the energy of photons at the threshold frequency.

(B) The lines for K and Ag do not begin at the same point because the amount of energy that an electron must absorb to leave the K atom is less than the amount of energy that an electron must absorb to leave the Ag atom, as the attraction between the nucleus and the nucleus is stronger in a Ag atom than in a K atom.

(C) Silver requires radiation of shorter wavelength (higher frequency) to eject an electron.

(D) The slopes of the lines show an increase in kinetic energy as the frequency (or energy) of light is increased. Since the slopes are the same, this means that for an increase of one unit of frequency of light, the

increase in kinetic energy of an electron ejected from K is the same as the increase in the kinetic energy of an electron ejected from Ag. Energy and frequency are linearly related, and the coefficient of proportionality is Planck's constant h.



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Problems researched and solved by Lucas Monteiro Nogueira. Edited by Lucas Monteiro Nogueira.