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## Constants and Conversion Factors

$N_{A}=6.02 \times 10^{23} \mathrm{~mol}^{-1}$
$\mathrm{R}=8.31 \mathrm{~J} / \mathrm{mol}-\mathrm{K}=8.31 \mathrm{kPa}-\mathrm{L} / \mathrm{mol}-\mathrm{K}$
$1 \mathrm{bar}=100 \mathrm{kPa}=750$ torr
$1 \mathrm{kPa}=7.50$ torr
$1 \mathrm{~J}=1 \mathrm{kPa}-\mathrm{L}$

1. A sample of decane, $\mathrm{C}_{10} \mathrm{H}_{22}(\mathrm{M}=142)$, contains $5.0 \times 10^{24}$ atoms of Hydrogen. What is the mass of the sample?
(A) 28.4 g
(B) 53.6 g
(C) 1180 g
(D) $2.6 \times 10^{4} \mathrm{~g}$
2. The pressure of a sample of $\mathrm{O}_{2}(\mathrm{~g})$ is 350 torr in a 50 L container at $400^{\circ} \mathrm{C}$. What is the pressure of this gas in a 20 L container at $100^{\circ} \mathrm{C}$ ?
(A) 1580 torr
(B) 485 torr
(C) 220 torr
(D) 78 torr
3. How many molecules of $\mathrm{CO}_{2}(\mathrm{M}=44)$ are contained in a 15 L container at $150^{\circ} \mathrm{C}$ and 1.0 bar?
(A) $7.2 \times 10^{23}$
(B) $2.6 \times 10^{21}$
(C) $5.8 \times 10^{22}$
(D) $2.6 \times 10^{23}$
4. A sample of $\mathrm{C}_{4} \mathrm{H}_{10}(\mathrm{~g})$ [ $\mathrm{M}=58$ ] effuses through a pinhole in 60. s . An equivalent amount of an unknown gas, $X$, effuses through the pinhole in 90 s . What is the approximate Molar Mass of the uinknown gas?
(A) $26 \mathrm{~g} / \mathrm{mol}$
(B) $45 \mathrm{~g} / \mathrm{mol}$
(C) $131 \mathrm{~g} / \mathrm{mol}$
(D) $87 \mathrm{~g} / \mathrm{mol}$
5. A 110 gram sample of $\mathrm{CO}_{2}(\mathrm{~g})(\mathrm{M}=44)$ is initially at $75^{\circ} \mathrm{C}$. When 5.0 kJ of heat is removed from the sample at constant pressure, the final temperature is $21^{\circ} \mathrm{C}$. The constant pressure molar heat capacity of $\mathrm{CO}_{2}$ is approximately:
(A) $28.8 \mathrm{~J} / \mathrm{mol}-\mathrm{K}$
(B) $51.7 \mathrm{~J} / \mathrm{mol}-\mathrm{K}$
(C) $92.6 \mathrm{~J} / \mathrm{mol}-\mathrm{K}$
(D) $37.0 \mathrm{~J} / \mathrm{mol}-\mathrm{K}$
6. When a gas is cooled at constant pressure, :
(A) $\mathrm{w}>0, \Delta \mathrm{H}<0$
(B) $\mathrm{w}<0, \Delta \mathrm{H}<0$
(C) $\mathrm{w}<0, \Delta \mathrm{H}>0$
(D) $\mathrm{w}=0, \Delta \mathrm{H}<0$
7. What are q and $\Delta \mathrm{H}$ when 2 moles of a gas is expanded reversibly and isothermally from 5 L to 40 L at $25^{\circ} \mathrm{C}$ ?
(A) $\mathrm{q}=-10.3 \mathrm{~kJ}, \Delta \mathrm{H}=0$
(B) $\mathrm{q}=+10.3 \mathrm{~kJ}, \Delta \mathrm{H}=0$
(C) $\mathrm{q}=0, \Delta \mathrm{H}=0$
(D) $\mathrm{q}=0, \Delta \mathrm{H}=+10.3 \mathrm{~kJ}$
8. Zinc reacts with Hydrochloric acid according to the reaction:
$\mathrm{Zn}(\mathrm{s})+\mathrm{HCl}(\mathrm{aq}) \rightarrow \mathrm{ZnCl}_{2}(\mathrm{aq})+\mathrm{H}_{2}(\mathrm{~g})$. What is the work, in kJ , when 1.5 moles of $\mathrm{Zn}(\mathrm{s})$ react with an excess of $\mathrm{HCl}(\mathrm{aq})$ at 1 bar and $30^{\circ} \mathrm{C}$ ?
(A) -3.8 kJ
(B) -2.5 kJ
(C) +3.8 kJ
(D) +2.5 kJ
9. What is the approximate work involved when 230 g of toluene, $\mathrm{C}_{7} \mathrm{H}_{8},(\mathrm{M}=92)$ is vaporized at 1 bar and $111{ }^{\circ} \mathrm{C}$ (its normal boiling point)?
(A) +2.3 kJ
(B) +87.9 kJ
(C) -8.0 kJ
(D) -2.3 kJ
10. The Enthalpy of Vaporization of toluene $(\mathrm{M}=92)$ is $38.1 \mathrm{~kJ} / \mathrm{mol}$. What iis the approximate value of the Internal Energy change, $\Delta \mathrm{U}$, when 230 g of toluene, $\mathrm{C}_{7} \mathrm{H}_{8}$, is vaporized at 1 bar and $111{ }^{\circ} \mathrm{C}$ (its normal boiling point)?
(A) +87.3 kJ
(B) 95.3 kJ
(C) 103.2 kJ
(D) -95.3 kJ
11. The constant pressure molar heat capacity of $\mathrm{CO}_{2}(\mathrm{~g})$ is $37.1 \mathrm{~J} / \mathrm{mol}-\mathrm{K}$. What is $\Delta \mathrm{S}$ when 3 moles of $\mathrm{CO}_{2}(\mathrm{~g})$ is cooled at constant pressure from $200^{\circ} \mathrm{C}$ to $50^{\circ} \mathrm{C}$ ?
(A) $9.5 \mathrm{~J} / \mathrm{K}$
(B) $-154.3 \mathrm{~J} / \mathrm{K}$
(C) $+154.3 \mathrm{~J} / \mathrm{K}$
(D) $-42.5 \mathrm{~J} / \mathrm{K}$
12. A sample of 0.5 moles of $\mathrm{O}_{2}(\mathrm{~g})$ originally at 500 kPa and 5 L is expanded reversibly and isothermally to a final volume of 25 L . What is $\Delta \mathrm{S}$ for this process?
(A) $+4030 \mathrm{~J} / \mathrm{K}$
(B) $+6.7 \mathrm{~J} / \mathrm{K}$
(C) $+13.4 \mathrm{~J} / \mathrm{K}$
(D) $-6.7 \mathrm{~J} / \mathrm{K}$
13. From the following thermochemical equations,

$$
\begin{array}{ll}
2 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \rightarrow 2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) & \Delta \mathrm{H}=+484 \mathrm{~kJ} \\
2 \mathrm{O}_{3}(\mathrm{~g}) \rightarrow 3 \mathrm{O}_{2}(\mathrm{~g}) & \Delta \mathrm{H}=+286 \mathrm{~kJ}
\end{array}
$$

$\Delta \mathrm{H}$ for the reaction, $3 \mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \rightarrow 3 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{3}(\mathrm{~g})$, is
(A) +583 kJ
(B) +341 kJ
(C) -583 kJ
(D) -869 kJ
14. The reaction, $A \rightarrow B$, is endergonic at $25^{\circ} \mathrm{C}$ and the entropy change is $+40 \mathrm{~J} / \mathrm{K}$. What can be concluded about the enthalpy change for this reaction?
(A) $\Delta \mathrm{H}>+11.9 \mathrm{~kJ}$
(B) $\Delta \mathrm{H}<-11.9 \mathrm{~kJ}$
(C) $\Delta \mathrm{H}>18.4 \mathrm{~kJ}$
(D) No conclusion can be made about $\Delta \mathrm{H}$
15. For the endergonic reaction, $\mathrm{C} \rightarrow \mathrm{D}, \Delta \mathrm{H}=-30 \mathrm{~kJ}$. For this reaction,
(A) $\Delta G>0$ and $\Delta S>0$
(B) $\Delta \mathrm{G}<0$ and $\Delta \mathrm{S}<0$
(C) $\Delta \mathrm{G}<0$ and $\Delta \mathrm{S}>0$
(D) $\Delta \mathrm{G}>0$ and $\Delta \mathrm{S}<0$
16. The normal melting point of toluene is $-95^{\circ} \mathrm{C}$. The enthalpy of fusion of toluene is $6.6 \mathrm{~kJ} / \mathrm{mol}$. What is the entropy change of the system when one mole of liquid toluene crystallizes to solid toluene at $-95^{\circ} \mathrm{C}$ ?
(A) $+69 \mathrm{~J} / \mathrm{mol}-\mathrm{K}$
(B) $-37 \mathrm{~J} / \mathrm{mol}-\mathrm{K}$
(C) $-69 \mathrm{~J} / \mathrm{mol}-\mathrm{K}$
(D) $+37 \mathrm{~J} / \mathrm{mol}-\mathrm{K}$
17. The Enthalpy of Fusion of acetone is $5.7 \mathrm{~kJ} / \mathrm{mol}$. The Entropy of Fusion of Acetone is $32.0 \mathrm{~J} / \mathrm{mol}-\mathrm{K}$. What is $\Delta \mathrm{G}$ when 1 mole of liquid acetone is crystallized to the solid at $20^{\circ} \mathrm{C}$ ?
(A) -3.7 kJ
(B) 0 kJ
(C) +3.7 kJ
(D) -15.1 kJ
18. When 30 grams of glucose $(\mathrm{M}=180)$ is added to 70 grams of water, the density of the solution is $1.20 \mathrm{~g} / \mathrm{mL}$. What is the Molarity of the solution?
(A) 1.4 M
(B) 1.7 M
(C) 2.0 M
(D) 2.4 M
19. When 42.4 grams of the strong electrolyte $\mathrm{K}_{3} \mathrm{PO}_{4}[\mathrm{M}=212]$ is dissolved in 100 grams of water ( $\mathrm{K}_{\mathrm{b}}=0.5^{\circ} \mathrm{C} / \mathrm{m}$ ), the boiling point of the solution is
(A) $96{ }^{\circ} \mathrm{C}$
(B) $104^{\circ} \mathrm{C}$
(C) $101{ }^{\circ} \mathrm{C}$
(D) $99{ }^{\circ} \mathrm{C}$
20. The normal boiling point of pure $\mathrm{CCl}_{4}(\mathrm{I})$ is $77^{\circ} \mathrm{C}$ and the boiling point elevation constant is $5.0^{\circ} \mathrm{C} / \mathrm{m}$. When 5 grams of an unknown compound is placed in 100 grams of $\mathrm{CCl}_{4}$, the boiling point of the solution is $84.5^{\circ} \mathrm{C}$. The Molar Mass of the unknown compound is approximately:
(A) $33 \mathrm{~g} / \mathrm{mol}$
(B) $64 \mathrm{~g} / \mathrm{mol}$
(C) $128 \mathrm{~g} / \mathrm{mol}$
(D) $3.3 \mathrm{~g} / \mathrm{mol}$
21. When 10. grams of glucose $(M=180)$ is dissolved in 200 mL of aqueous solution, the osmotic pressure at $100^{\circ} \mathrm{C}$ is:
(A) 1.7 bar
(B) 860 bar
(C) 2.3 bar
(D) 8.6 bar

For \#22 - \#26: Consider the gas phase equilibrium, $4 \mathrm{NO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \leftrightharpoons 2 \mathrm{~N}_{2} \mathrm{O}_{5}(\mathrm{~g})$. The enthalpy change for this reaction is $\Delta \mathrm{H}^{0}-340 \mathrm{~kJ}$, and the equilibrium constant is $\mathrm{K}=8$ at $175{ }^{\circ} \mathrm{C}\left(\Delta \mathrm{G}^{\circ}-7.74 \mathrm{~kJ}\right)$.
22. For the above reaction, if the volume of the container is increased,
(A) the equilibrium will move to the left and $K$ will decrease
(B) the equilibrium will move to the right and $K$ will increase
(C) the equilibrium will move to the left and K will remain constant
(D) the equilibrium will move to the right and K will remain constant
23. For the above reaction, if the temperature is increased,
(A) the equilibrium will move to the left and K will decrease
(B) the equilibrium will move to the right and $K$ will increase
(C) the equilibrium will move to the left and K will remain constant
(D) the equilibrium will move to the right and K will remain constant
24. What is $\Delta G$ for this reaction at $175{ }^{\circ} \mathrm{C}$ when the pressures are: $\mathrm{P}\left(\mathrm{NO}_{2}\right)=0.5 \mathrm{bar}$, $\mathrm{P}\left(\mathrm{O}_{2}\right)=0.3$ bar and $\mathrm{P}\left(\mathrm{N}_{2} \mathrm{O}_{5}\right)=2.0$ bar?
(A) -27.7 kJ
(B) -7.7 kJ
(C) +20.0 kJ
(D) +12.2 kJ
25. What is the approximate value of the equilibrium constant, K , for the above reaction at $150^{\circ} \mathrm{C}$ ?
(A) 220
(B) 1770
(C) $3.6 \times 10^{-2}$
(D) $4.5 \times 10^{-3}$
26. What is K for the reaction, $\mathrm{N}_{2} \mathrm{O}_{5} \leftrightharpoons 2 \mathrm{NO}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g})$ at $175^{\circ} \mathrm{C}$.
(A) 0.35
(B) 0.25
(C) 2.8
(D) 4.0
27. For the gas phase equilibrium, $2 \mathrm{~A}(\mathrm{~g})+\mathrm{B}(\mathrm{g}) \leftrightharpoons 2 \mathrm{C}(\mathrm{g})$, the equilibrium constant is $K=1 \times 10^{-3}$. If one puts $A$ and $B$ into a vessel with initial pressures, $P_{\text {init }}(A)=P_{\text {init }}(B)=$ 3. bar, what is the pressure of $C$ at equililbrium?

NOTE: You may assume that very little $A$ and $B$ react.
(A) 0.045 bar
(B) 0.164 bar
(C) 0.082 bar
(D) 0.063 bar

For \#28-\#29: Hydrocyanic acid, HCN, is a weak acid with acid dissociation constant, $K a=5.0 \times 10^{-10}$.
28. What is the pH of 0.2 M potassium cyanide, KCN ?
(A) 2.7
(B) 5.0
(C) 9.0
(D) 11.3
29. What is the pH of 2 Liters of 0.3 M KCN following the addition of 0.2 mol of HCl ?
(A) 5.0
(B) 9.0
(C) 9.6
(D) 9.8

For \#30-\#33: Consider the dipeptide (Pep) consisting of an Aspartic Acid residue and a Cysteine residue (pictured on right)

The two side groups ionize according to:

$-\mathrm{CH}_{2} \mathrm{CO}_{2} \mathrm{H} \leftrightharpoons \mathrm{H}^{+}+-\mathrm{CH}_{2} \mathrm{CO}_{2}^{-}$and $-\mathrm{CH}_{2} \mathrm{SH} \leftrightharpoons \mathrm{H}^{+}+-\mathrm{CH}_{2} \mathrm{~S}^{-}$
The four $\mathrm{pK}_{\mathrm{a}}$ 's are: $\mathrm{pK}_{\mathrm{a}}{ }^{\prime}\left(\alpha-\mathrm{CO}_{2} \mathrm{H}\right)=1.9, \mathrm{pK}_{\mathrm{a}}{ }^{\prime \prime}\left(\beta-\mathrm{CO}_{2} \mathrm{H}\right)=3.9, \mathrm{pK}_{\mathrm{a}}{ }^{\prime \prime}{ }^{\prime}\left(\mathrm{CH}_{2} \mathrm{SH}\right)=8.5$ and $\mathrm{pK}_{\mathrm{a}}{ }^{\prime \prime \prime \prime}\left(\alpha-\mathrm{NH}_{3}{ }^{+}\right)=9.9$
30. What is the pH after 2.0 equivalents of NaOH are added to a solution containing the most acidic form of Pep?
(A) 2.9
(B) 3.9
(C) 6.2
(D) 8.5
31. What pH corresponds to the isoelectric point, pl , of Pep?
(A) 2.9
(B) 3.9
(C) 6.2
(D) 9.2
32. What is the average charge of Pep at $\mathrm{pH}=8.5$ ?
(A) -1.5
(B) -0.5
(C) -2.0
(D) -2.5
33. What form of the peptide is present in highest concentration in a Pep solution buffered to $\mathrm{pH}=5.0$ ?
(A) $\mathrm{Pep}^{1+}$
(B) Pep
(C) $\mathrm{Pep}^{1-}$
(D) $P e p^{2-}$
34. The reaction, $A \rightarrow$ Products, is of order " $x$ "; therefore, the initial rate, $r_{o}=k[A]_{0}{ }^{x}$. When $[A]_{0}=0.2 \mathrm{M}, \mathrm{r}_{0}=0.10 \mathrm{M} / \mathrm{s}$. When $[\mathrm{A}]_{0}=0.8 \mathrm{M}, \mathrm{r}_{0}=6.40 \mathrm{M} / \mathrm{s}$. Therefore, the reaction order, x , is
(A) 1.0
(B) 2.5
(C) 2.0
(D) 3.0
35. Consider a second order reaction, rate $=k[A]^{2}$, with a rate constant, $k=0.03 \mathrm{M}^{-1} \mathrm{~s}^{-1}$. If one starts with an initial concentration, $[\mathrm{A}]_{\mathrm{o}}=0.80 \mathrm{M}$, approximately how long will it take for the concentration of A to decrease to 0.30 M ?
(A) 70 s
(B) 140 s
(C) 35 s
(D) 320 s
36. Consider a zeroth order reaction, rate $=k[A]^{0}=k$, When the initial concentration of $A$ is 0.70 M , the hallf life of the reaction is 5.0 s . What is the approximate value of the rate constant for this zeroth order reaction?
(A) $0.14 \mathrm{Ms}^{-1}$
(B) $0.07 \mathrm{Ms}^{-1}$
(C) $0.29 \mathrm{Ms}^{-1}$
(D) $0.035 \mathrm{Ms}^{-1}$
37. The reaction, $2 \mathrm{NO}+\mathrm{O}_{2} \rightarrow 2 \mathrm{NO}_{2}$, proceeds by a two step mechanism:
(1) $2 \mathrm{NO} \square \mathrm{N}_{2} \mathrm{O}_{2}$ (fast pre-equilibrium characterized by the equilibrium constant, K),
(2) $\mathrm{N}_{2} \mathrm{O}_{2}+\mathrm{O}_{2} \rightarrow 2 \mathrm{NO}_{2}$ (slow rate-determining step, characterized by the rate constant, k ). The rate law for the formation of product is of the form:
(A) $\mathrm{keff}[\mathrm{NO}]\left[\mathrm{O}_{2}\right]$
(B) $\mathrm{K}_{\text {eff }}\left[\mathrm{N}_{2} \mathrm{O}_{2}\right]\left[\mathrm{O}_{2}\right]^{2}$
(C) $\mathrm{keff}[\mathrm{NO}]^{1 / 2}\left[\mathrm{O}_{2}\right]$
(D) $\mathrm{K}_{\mathrm{eff}}[\mathrm{NO}]^{2}\left[\mathrm{O}_{2}\right]$

For \#38-\#39: Consider an enzyme catalyzed reaction for which the slope and intercept of the Lineweaver-Burk (double reciprocal) plot are: Slope= 0.02 s , Intercept $=0.01(\mathrm{mM})^{-1} \mathrm{~s}$.

38 For this reaction, the maximum velocity, $\mathrm{V}_{\mathrm{m}}$, is
(A) $0.5 \mathrm{mM} \mathrm{s}^{-1}$
(B) $100 \mathrm{mM} \mathrm{s}^{-1}$
(C) $50 \mathrm{mM} \mathrm{s}^{-1}$
(D) $2.0 \mathrm{mM} \mathrm{s}^{-1}$
39. For this reaction, the Michaelis constant, $\mathrm{K}_{\mathrm{M}}$, is
(A) 0.002 mM
(B) 0.50 mM
(C) 2.0 mM
(D) 500 mM
40. For an enzyme catalyzed reaction, $\mathrm{V}_{\mathrm{m}}=50 \mathrm{mM} / \mathrm{s}$ and $[\mathrm{E}]_{0}=0.05 \mathrm{mM}$. Therefore, the "turnover number", $\mathrm{k}_{2}$, is
(A) $1000 \mathrm{~s}^{-1}$
(B) 0.001 s
(C) $0.4 \mathrm{~s} / \mathrm{mM}$
(D) $2.5 \mathrm{mM} / \mathrm{s}$
41. When an inhibitor is added to an enzyme catalyzed reaction, it is found that the intercept of the Lineweaver-Burk plot is increased, but the slope is not affected. Therefore, the type of inhibition is
(A) Uncompetitive
(B) Noncompetitive
(C) Competitive
(D) Briggs-Haldane

For \#42-\#43: Consider an enzyme catalyzed reaction with $\mathrm{K}_{\mathrm{m}}=40 \mathrm{mM}, \mathrm{V}_{\mathrm{m}}=150 \mu \mathrm{M} / \mathrm{s}$, and $[\mathrm{S}]=80 \mathrm{mM}$. An Uncompetitive inhibitor to this reaction has an inhibitor constant, $\mathrm{K}_{\mathrm{I}}=20 \mathrm{mM}$.
42. What is the initial velocity, $\mathrm{v}_{\mathrm{o}}$, in the absence of the inhibitor?
(A) $50 \mu \mathrm{M} / \mathrm{s}$
(B) $120 \mu \mathrm{M} / \mathrm{s}$
(C) $100 \mu \mathrm{M} / \mathrm{s}$
(D) $225 \mu \mathrm{M} / \mathrm{s}$
43. What is the percent inhibition (i\%) when the inhibitor concentration is [I]= 50 mM ?
(A) $38 \%$
(B) $45 \%$
(C) $71 \%$
(D) $63 \%$
(30) PART II. THREE (3) PROBLEMS FOLLOW (Show work for partial credit)
(08) 1. The reaction, $2 C+D \rightarrow P(P$ is the product) proceeds by the following mechanism:

$$
\mathrm{C}+\mathrm{D} \underset{\mathrm{k}_{-1}}{\mathrm{k}_{1}} \mathbf{I} \quad \text { followed by } \quad \mathbf{I}+\mathrm{C} \xrightarrow{\mathrm{k}_{2}} \mathrm{P}
$$

" $\mathbf{I}$ " is an intermediate present in steady-state concentration. Use the steady-state approximation on $[\mathbf{I}]$ to develop an expression for the rate of formation of P as a function of [C], [D], $\mathrm{k}_{1}, \mathrm{k}_{-1}$ and $\mathrm{k}_{2}$.
(12) 2. The rate constant for a first order reaction is $0.20 \mathrm{~s}^{-1}$ at $30^{\circ} \mathrm{C}$ and $12.40 \mathrm{~s}^{-1}$ at $100^{\circ} \mathrm{C}$.
Calculate the Activation Energy, $\mathrm{E}_{\mathrm{a}}$ (in $\mathrm{kJ} / \mathrm{mol}$ ) and the Pre-Exponential Factor, A (in s${ }^{-1}$ ) for this reaction.
(10) 3. An enzyme has the Michaelis-Menten parameters, $\mathrm{K}_{\mathrm{M}}=8.0 \times 10^{-4} \mathrm{M}$ and $\mathrm{V}_{\mathrm{m}}=80 \mathrm{mM} / \mathrm{min}$. The inhibition equilibrium constant for Competitive inhibition is $\mathrm{K}_{\mathrm{I}}=2.5 \times 10^{-4} \mathrm{M}$. When [S]= $1.0 \times 10^{-3} \mathrm{M}$, calculate the inhibitor concentration, [I], required to get $80 \%$ inhibition (i.e. i\%=80) for this Competitive inhibitor.

