INFORMATION PAGES (Use for reference and for scratch paper)

Constants and Conversion Factors:

R = 8.31 J/mol-K = 8.31 kPa-L/mol-K = 0.00831 kJ/mol-K

1 L-atm = 101 J	1 L-bar = 100 J
1 kPa-L = 1 J	1 bar = 100 kPa
1 atm = 760 torr	1 bar = 750 torr

Relations for Adiabatic Expansions and Compressions of a Perfect Gas

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/C_{V,m}} \quad \text{or} \quad \frac{p_2}{p_1} = \left(\frac{V_1}{V_2}\right)^{C_{p,m}/C_{V,m}} = \left(\frac{V_1}{V_2}\right)^{\gamma}$$

The TST Equation: $k = \dfrac{RT}{N_A h} e^{\frac{\Delta S^{\pm}}{R}} e^{\frac{-\Delta H^{\pm}}{RT}}$ R, N_A and h are universal constants:

where: $\dfrac{R}{N_A h} = \dfrac{8.31}{(6.02x10^{23})(6.63x10^{-34})} = 2.1x10^{10}$

Photochemistry equations on following page.

Photochemistry

Singlet State Lifetime: $\tau_0 = \dfrac{1}{k_0} = \dfrac{1}{k_F + k_{IC} + k_{ISC}}$

Fluorence Quantum Yield (No quencher):

$$\Phi_{F,0} = \dfrac{k_F}{k_F + k_{IC} + k_{ISC}} = \dfrac{k_F}{k_0}$$

Fluorescence Quantum Yield (quencher, Q, present): - NOT NEEDED THIS YEAR

$$\Phi_F = \dfrac{k_F}{k_F + k_{IC} + k_{ISC} + k_Q[Q]} = \dfrac{k_F}{k_0 + k_Q[Q]}$$

Light Energy/Wavelength Relation: $E_{ph} = h\nu = \dfrac{hc}{\lambda(m)} = \dfrac{1.99 \times 10^{-25}\, J \cdot m}{\lambda(m)}$

Name _Solutions_

If you wish to have your final exam and course grade posted on the Web site, please provide me with a four (4) digit number which will be the ID number for your grade.

_____

Four (4) digit number for posting

(78) MULTIPLE CHOICE [3 points per question] (Circle the ONE correct answer)

1. Dimanganese Decacarbonyl can be decomposed to CO(g) and Mn(s) via the reaction: $Mn_2(CO)_{10}(s) \rightarrow 2Mn(s) + 10CO(g)$

   What is the work involved when a sufficient quantity of $Mn_2(CO)_{10}(s)$ is decomposed to form three(3) moles of Mn(s) at 200 °C and 1. bar pressure (in kJ)?

   (A) -59.0 kJ   (B) -24.9 kJ   (C) +39.3 kJ   (D) -39.3 kJ

2. The constant volume molar heat capacity of $CO_2(g)$ is constant at $C_{V,m}$ = 28.2 J/mol-K. When 5. moles of $CO_2(g)$ is cooled from 300 °C to 50 °C at a constant pressure of 1. bar, the enthalpy change and work are approximately:

   (A) ΔH = -45.6 kJ & w = -10.4 kJ   (B) ΔH = -35.3 kJ & w = +10.4 kJ

   (C) ΔH = -45.6 kJ & w = +10.4 kJ   (D) ΔH = -35.3 kJ & w = -10.4 kJ

For #3 - #4: Consider **four(4)** moles of a perfect gas initially at a temperature of 300 °C and volume of 20 L. The gas has a **constant volume** molar heat capacity, $C_{V,m}$ = 25.7 J/mol-K. The gas undergoes a **reversible, adiabatic** expansion to a final volume of 50 L.

3. The work, w, for this process is approximately:

   (A) -11.8 kJ   (B) -7.9 kJ   (C) 0 kJ   **(D) -15.1 kJ**

4. The Enthalpy change, ΔH, for this process is approximately:

   (A) -15.6 kJ   **(B) -20.0 kJ**   (C) -26.4 kJ   (D) -10.5 kJ

For #5 - #7: The boiling point of p-dibromobenzene is 220 °C and the Enthalpy of Vaporization is 50.0 kJ/mol. Consider the reversible condensation of **six(6)** moles of p-dibromobenzene at 220 °C and 1 bar pressure.

5. The work, w, for this process is approximately

    (A) -11.0 kJ   (B) +24.6 kJ   (C) -24.6 kJ   (D) +11.0 kJ

6. The Internal Energy change, ΔU , for this process is approximately

    (A) -325 kJ   (B) +325 kJ   (C) -275 kJ   (D) 0 kJ

7. The entropy change of the system, ΔS_{sys}, for this process is approximately

    (A) -610 J/K   (B) -100 J/K   (C) 0 J/K   (D) +610 J/K

8. The normal melting point of toluene is -95 °C. The Enthalpy of Fusion of toluene is 6.6 kJ/mol. What is the approximate entropy change of the surroundings, ΔS_{surr}, when **three(3)** moles of liquid toluene crystallize to solid toluene at -95 °C?

    (A) -54 J/K   (B) -111 J/K   (C) +37 J/K   (D) +111 J/K

9. When 20 grams of an unknown compound is dissolved in 150 grams of water (K_f = 1.86 °C/m), the freezing point of the solution is -3.5 °C. What is the Molar Mass of the unknown compound?

    (A) 10.6 g/mol   (B) 71. g/mol   (C) 124.. g/mol   (D) 45. g/mol

    For #10 - #13: Consider the gas phase equilibrium,
    $2 NO_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons N_2O_5(g)$. The enthalpy change for this reaction is -170. kJ and the equilibrium constant is 2.5 at 150 °C.

10. For the above reaction, if $N_2(g)$ is added at a constant total pressure of 5 bar,

    (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

11. 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

12. The Gibbs energy change, $\Delta_r G$, for the above reaction at 150 °C when $P_{N2O5} = 2.0$ bar and $P_{NO2} = P_{O2} = 0.80$ bar is approximately

    (A) -3.2 kJ   (B) -7.6 kJ   (C) +7.6 kJ   (D) +1.2 kJ

13. The value of the equilibrium constant for the above reaction at 100 °C is approximately:

    (A) 1630.   (B) 650.   (C) 2.52   (D) 6.1×10^{-4}

14. Consider the gas phase equilibrium, $A(g) \rightleftharpoons 2B(g)$. When the pressures of A and B are each 0.30 bar at 100 °C, the Gibbs Energy change for the reaction is -1.50 kJ. What is the approximate value of the equilibrium constant?

    (A) 5.4   (B) 0.5   (C) 2.1   (D 0.3

15. Radioisotope decay follows **first order** kinetics. Radioiodine (^{131}I) is used in the medical treatment of hyperthyroidism. The first order rate constant for the decays of the ^{131}I isotope is 0.087 days^{-1}. If a 50 mg sample of radioiodine is administered to a patient, how long will it take for the amount of radioiodine to decrease to 10 mg?

    (A) 26.4 days   (B) 20.7 days   (C) 18.5 days   (D) 11.3 days

For #16 - #17: Consider the reaction, A → P, which is a 3/2 order reaction; i.e. rate = $k[A]^{3/2}$. The rate constant for this reaction is k= 0.02 M$^{-1/2}$s^{-1}, and the initial concentration of A is 0.60 M.

16. What is the half-life of this reaction?

    (A) 17 s   (B) 27 s   (C) 13 s   (D) 53 s

17. What will be the concentration of [A] 40 s after the start of the reaction.

    (A) 0.35 M   (B) 0.23 M   (C) 0.12 M   (D) 0.42 M

18. The reaction, A → P, is of order "x"; i.e. rate = $k[A]^x$. When $[A_o] = 0.6$ M, the half-life of the reaction is 150. s. When $[A]_o = 0.2$ M, the half life of the reaction is 260. s. The order of the reaction, x, is

    (A) 1/2   (B) 3   (C) 3/2   (D) 5/2

19. Consider a fourth order reaction, A → Products, $-\dfrac{d[A]}{dt} = k[A]^4$

    When the initial concentration of A is 0.15 M, the initial rate is 0.030 Ms^{-1}. The rate constant for this reaction, k, is approximately

    (A) 0.012 M^{-3}s^{-1} (B) 60. M^{-3}s^{-1} (C) 1.5×10^{-5} M^{-3}s^{-1} (D) 8.9 M^{-3}s^{-1}

20. When a standard TST Analysis was carried out on temperature dependent rate constant data, it was determined that the Entropy of Activation for the reaction was +85 J/mol-K. Therefore, the intercept of the standard TST plot was:

Note: The Transition State Theory (TST) equation in on the information sheet.

(A) -13.5 (B) +108.8 (C) +34.0 (D) +13.5

For #21 - #22: Consider a hypothetical theory of the rate constant, in which k is of the form: $k = CT^{3/2}e^{-\frac{E_0}{RT}}$, where C is a constant and E_0 is the "Threshold Energy".
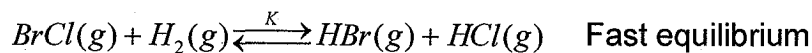
21. If one has rate constants, k, as a function of temperature, T, what would one plot in order to obtain a straight line using this theory?

(A) $\ln(k/T)$ vs. $1/T$ (B) $\ln(k/T^{3/2})$ vs. $1/T$

(C) $\ln(k/T^{1/2})$ vs. $1/T$ (D) $\ln(k \bullet T^{3/2})$ vs. $1/T$

22. If a given reaction is of the form given above, and you are told that the **Arrhenius Activation Energy, E_a,** is 130. kJ/mol, then at 1000 °C, the **"Threshold Energy", E_0,** is approximately:

(A) 117.5 kJ/mol   (B) 145.9 kJ/mol   (C) 119.4 kJ/mol   (D) 114.1 kJ/mol

23. For the reaction, 2 BrCl(g) + H_2(g) → 2 HCl(g) + Br_2(g), the reaction mechanism is:

$$BrCl(g) + H_2(g) \underset{}{\overset{K}{\rightleftharpoons}} HBr(g) + HCl(g) \quad \text{Fast equilibrium}$$

$$HBr(g) + BrCl(g) \overset{k}{\longrightarrow} HCl(g) + Br_2(g) \quad \text{Slow step}$$

An acceptable overall rate equation for the formation of Br_2, $\dfrac{d[Br_2]}{dt}$, is:

(A) $Rate = k'\dfrac{[BrCl]^2[H_2]}{[HCl]}$ (B) $Rate = k'[BrCl][H_2]$

(C) $Rate = k'[HBr][BrCl]$ (D) $Rate = k'\dfrac{[BrCl][H_2]}{[HCl]}$

24. In a photochemical reaction, $A \rightarrow 2\,B + C$, the reaction quantum yield for the decomposition of A is $\Phi_R = 0.45$. A absorbs radiation at a rate of $5. \times 10^{19}$ absorbed photons per second for a total of 90 minutes. Approximately how many moles of B have been formed by the end of the irradiation period?

*The numerical value of λ is unnecessary to work the question.

(A) 0.10 mol   (B) 0.49 mol   (C) 0.20 mol   (D) 0.40 mol

For #25 - #26: In a **pulsed** laser fluorescence experiment on an organic chromophore, the fluorescence intensity 45 ns after the experiment begins is 70% of the intensity at the start of the experiment.

In a separate steady-state fluoescence experiment, it was determined that the fluorescence rate constant is: $k_F = 3.4 \times 10^6\ s^{-1}$

25. The singlet state lifetime of the chromophore, τ_0, is approximately:

(A) 37 ns   (B) 126 ns   (C) 290 ns   (D) 16 ns

26. The fluorescence quantum yield of the chromophore is approximately:

(A) 0.43   (B) 2.3   (C) 0.68   (D) 0.13

There are six (6) problems following. You must show your work to receive credit.

(10) 1. A Perfect Gas has a temperature dependent **constant pressure** molar heat capacity, $C_{p,m} = a + bT^2$, with a = 22 J/mol-K and b = 1.5x10^{-5} J/mol-K^3.

Three (3) moles of this gas, originally at 600 °C and 1.5 atm is cooled reversibly at **constant volume** to 200 °C.

Calculate the Internal Energy change, ΔU, for this process, in kJ.

$$C_{v,m} = C_{p,m} - R = a + bT^2 - R$$

$$= (a - R) + bT^2 = a' + bT^2$$

$$a' = a - R$$
$$= 22 - 8.31$$
$$= 13.7 \ J/mol\text{-}K$$

$$T_1 = 600°C = 873 \ K \qquad n = 3 \ mol.$$
$$T_2 = 200°C = 473 \ K$$

$$\Delta U = \int_{T_1}^{T_2} n \, C_{v,m} \, dT = \int_{T_1}^{T_2} n(a' + bT^2) \, dT$$

$$= na'[T_2 - T_1] + \frac{nb}{3}[T_2^3 - T_1^3]$$

$$= 3 \ mol \, (13.7 \ J/mol\text{-}K)(473K - 873K) + \frac{3 \ mol \, (1.5 \times 10^{-5} \ J/mol\text{-}K^3)}{3}(473^3 - 873^3)$$

$$= -16440 \ J + (-8390 \ J)$$

$$= -24,830 \ J \approx \boxed{-24.8 \ kJ}$$

(10) 2. Consider a hypothetical gas that obeys the equation of state:

$$p(V - Bp^2) = nRT \longrightarrow V = \frac{nRT}{p} + Bp^2$$

If this gas undergoes an isothermal compression from p_1 to p_2, develop **INTEGRATED** expressions for ΔU and ΔA in terms of n, R, T, B, p_1 and p_2.

$$dU = TdS - pdV$$

$$\left(\frac{\partial U}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T - p\left(\frac{\partial V}{\partial p}\right)_T$$

$$= T\left(-\frac{nR}{p}\right) - p\left[\frac{-nRT}{p^2} + 2Bp\right]$$

$$= -\frac{nRT}{p} + \frac{nRT}{p} - 2Bp^2 = -2Bp^2$$

$$\Delta U = \int_{p_1}^{p_2}\left(\frac{\partial U}{\partial p}\right)_T dp = \int_{p_1}^{p_2} -2Bp^2 \, dp = \boxed{-\frac{2B}{3}\left(p_2^3 - p_1^3\right)}$$

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p} \qquad \left(\frac{\partial V}{\partial p}\right)_T = -\frac{nRT}{p^2} + 2Bp$$

$$dG = -SdT + Vdp \to \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

$$= -\frac{nR}{p}$$

$$dA = -SdT - pdV$$

$$\left(\frac{\partial A}{\partial p}\right)_T = 0 - p\left(\frac{\partial V}{\partial p}\right)_T = -p\left(-\frac{nRT}{p^2} + 2Bp\right) = \frac{nRT}{p} - 2Bp^2$$

$$\Delta A = \int_{p_1}^{p_2}\left(\frac{\partial A}{\partial p}\right)_T dp = \int_{p_1}^{p_2}\left(\frac{nRT}{p} - 2Bp^2\right) dp$$

$$= nRT \ln\left(\frac{p_2}{p_1}\right) - \frac{2B}{3}\left(p_2^3 - p_1^3\right)$$

$$T_1 = 145°C = 418K \text{ (actual trans. T)}$$
$$T_2 = 125°C = 398K \text{ (normal trans. T)}$$

(10) 3. The normal boiling point of octane is 125 °C.
The Enthalpy of Vaporization of octane is 34.4 kJ/mol at 125 °C.
The constant pressure molar heat capacity of liquid octane is 240. J/mol-K.
The constant pressure molar heat capacity of octane gas is 180 J/mol-K.

Calculate the entropy change of the **Surroundings**, ΔS_{surr} , (in J/mol-K) when $\Delta_{vp} H°(T_1)$ one (1) mole of super heated liquid octane vaporizes irreversibly at 145 °C.

Have $\Delta_{vp} H°(T_2 = 398K)$.

Need $\Delta_{vp} H°(T_1 418K)$
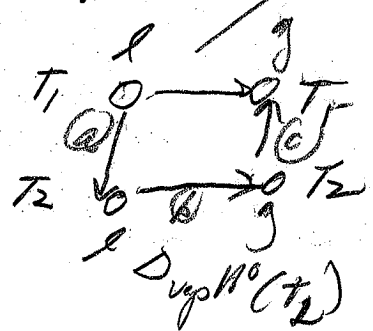
$$\Delta_{vp} H°(T_1 = 418K) = \Delta H_a + \Delta H_b + \Delta H_c$$

$$= C_{pm}(\ell)[T_2 - T_1] + \Delta_{vp} H°(T_2 = 398K) + C_{pm}(g)[T_1 - T_2]$$

Cool to BP = 398K   Vaporize   Heat to 418K

$$= 240[398 - 418] + 34.4 \times 10^3 + 180[418 - 398]$$

$$= -4800 \, J + 34,400 \, J + 3600 \, J$$

$$= 33,200 \, J \text{ — this is } \Delta_{vp} H°(T_1 = 418K) = q_{sys}.$$

$$q_{sur} = -q_{sys} = -33,200 \, J$$

$$\Delta S_{sur} = \frac{q_{sur}}{T_1} = \frac{-33,200 \, J}{418K} = \boxed{-79.4 \, J/K}$$

$$k_1 = 85\ s^{-1} \quad T_1 = 50°C = 323\ K$$
$$k_2 = 3200\ s^{-1} \quad T_2 = 150°C = 423°$$

(10) 4. Consider a first order reaction for which the the rate constant is 85. s⁻¹ at 50 °C and 3200. s⁻¹ at 150 °C.

Calculate the Arrhenius pre-exponential factor, A (in s⁻¹), for this reaction.

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$
$$\ln k_2 = \ln A - E_a/RT_2 \qquad \rightarrow \qquad \ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$E_a = \frac{-R\ln\left(\frac{k_2}{k_1}\right)}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{-8.31\ \ln\left(\frac{3200}{85}\right)}{\frac{1}{423} - \frac{1}{323}}$$

$$= 41,200\ J/mol$$

$$\ln A = \ln k_1 + \frac{E_a}{RT_1} = \ln 85 + \frac{41,200}{8.31(323)} =$$

$$= 19.79$$

$$\boxed{A = e^{19.79} = 3.9 \times 10^{8}\ s^{-1}}$$

get same value of A using k_2, T_2

(10) 5. The reaction, $2B + C \rightarrow P$ (P is the product) proceeds by the following mechanism.

$$B + C \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I \qquad \text{followed by} \qquad B + I \overset{k_2}{\longrightarrow} P$$

"**I**" is an intermediate present in steady-state concentration. Use the steady-state approximation on [**I**] to develop an expression for the rate of formation of P as a function of [B], [C], k_1, k_{-1} and k_2.

$$\frac{d[P]}{dt} = k_2[B][I] = k_2[B]\left(\frac{k_1[B][C]}{k_{-1} + k_2[B]}\right)$$

$$= \boxed{\frac{k_1 k_2 [B]^2 [C]}{k_{-1} + k_2[B]}}$$

steady-state on [I]

$$\frac{d[I]}{dt} = 0 = k_1[B][C] - k_{-1}[I] - k_2[B][I]$$

$$= k_1[B][C] - [I]\left(k_{-1} + k_2[B]\right)$$

$$\therefore \quad [I] = \frac{k_1[B][C]}{k_{-1} + k_2[B]}$$

6.

(10) 6. The fluorescence quantum yield for a given chromophore, A, has been determined to be $\Phi_F = 0.60$. A sample of A is irradiated with 260 nm radiation from a 150 W (J/s) for a period of 1 hour. The intensity of the **transmitted** light is 30% that of the incident light.

How many moles of the sample, A, have fluoresced in the 1 hour period?

Calc of n_{ph} (incid)

$$E_{ph} = 150 \frac{J}{s} \times \frac{60\,s}{1\,min} \times \frac{60\,min}{1\,hr} \times 1\,hr = 5.40 \times 10^5 J$$

$$E_{ph} = \frac{1.99 \times 10^{-25}\,J\cdot m}{260 \times 10^{-9}\,m} = 7.65 \times 10^{-19}\,J$$

$$n_{ph}(incid) = \frac{E_{tot}}{E_{ph}} = \frac{5.4 \times 10^5}{7.65 \times 10^{-19}} = 7.06 \times 10^{23}\,ph.$$

$$n_{ph}(incid) = 7.06 \times 10^{23} \times \frac{1\,mol}{6.02 \times 10^{23}} = 1.17\,mol$$

Calc of n_{ph} (abs)

$$n_{ph}(abs) = n_{ph}(incid)[1 - f(trans)]$$

$$= 1.17\,mol\,(1 - 0.30) = 0.82\,mol.$$

$$\Phi_R = \frac{n_A}{n_{ph}(abs)} \rightarrow n_A = \Phi_R(n_{ph}(abs))$$

$$= 0.60\,(0.82)$$

$$= \boxed{0.49\,mol\ A\ fluoresce}$$