Chemistry 431
Practice Final Exam
Fall 2023
Solutions

$R =$ 8.3144 J mol^{-1} K^{-1}

$R=$.0821 L atm mol^{-1} K^{-1}

$R=$.08314 L bar mol^{-1} K^{-1}

$k=$1.381 $\times 10^{-23}$ J molecule^{-1}K^{-1}

$h=$6.626 $\times 10^{-34}$ Js

$N_A = 6.022 \times 10^{23}$ molecules mol^{-1}

$F=$96485 C mol^{-1}

$g=$9.8 m s^{-2}

1 atmosphere $= 1.01$ bar $= 1.01 \times 10^5$ N m^{-2}

1 kg $= 1000.$ g

1 L $= 10^3$ cm^3

10^2 cm $= 1$ m

$\sigma = 4\pi r^2 \qquad V = (4/3)\pi r^3$

$T = t + 273.15$

$1 + x + x^2 + x^3 + \ldots = 1/(1-x) \qquad |x| < 1$

Each question is worth 33 Points. Writing your correct name on the cover and on all pages with work is worth 2 points.

Name:

1. Calculate $q, w, \Delta U, \Delta H$ and ΔS when 3.50 moles of an ideal monatomic gas initially at a temperature of $T_i = 298$ K and a pressure of $P_i = 1.00$ bar are taken though the following two-step process: 1) the gas is compressed adiabatically and reversibly until the volume is 0.750 times the initial volume, and 2) the gas expands adiabatically against a constant external pressure of 1.00 bar until equilibrium is reached.

Answer:

$$q = 0$$

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1} \qquad T_2 = 298K \left(\frac{1}{0.750}\right)^{2/3} \qquad T_2 = 361K$$

$$w = \Delta U = -P_{ext}\Delta V = -1.00 \left(\frac{nRT_f}{1.00} - \frac{nR(361 \text{ K})}{P_2}\right) = C_V \Delta T = \frac{3}{2}nR(T_f - 361 \text{ K})$$

$$P_2 = \frac{nRT_2}{V_2} = \frac{nR(361)}{nR(298)(0.75)/1.00 \text{ bar}} = 1.61 \text{ bar}$$

$$-T_f + \frac{361 \text{ K}}{1.61} = \frac{3}{2}(T_f - 361 \text{ K}) \qquad T_f = 306 \text{ K}$$

$$\Delta U = w = \frac{3}{2}nR\Delta T = \frac{3}{2}(3.50 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(306 \text{ K} - 298 \text{ K}) = 349 \text{ J}$$

$$\Delta H = \frac{5}{3}\Delta U = 582 \text{ J}$$

$$\Delta S = C_P \ln \frac{T_f}{T_i} = \frac{5}{2}nR \ln \frac{T_f}{T_i} = \frac{5}{2}(3.50 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1}) \ln \frac{306}{298} = 1.93 \text{ J K}^{-1}$$

Name:

2. Show that
$$\left(\frac{\partial U}{\partial T}\right)_S = \frac{C_V P}{T(\partial P/\partial T)_V}$$
and evaluate the expression for an ideal monatomic gas.

Answer:

$$dU = TdS - PdV$$

$$\left(\frac{\partial U}{\partial T}\right)_S = -P\left(\frac{\partial V}{\partial T}\right)_S$$

$$\left(\frac{\partial V}{\partial T}\right)_S \left(\frac{\partial T}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T = -1$$

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

$$dS = \frac{1}{T}dU + \frac{P}{T}dV \qquad \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

$$dA = -SdT - PdV \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial V}{\partial T}\right)_S = \frac{C_V}{\left(\frac{\partial P}{\partial T}\right)_V}$$
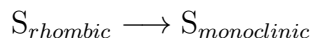
$$\left(\frac{\partial U}{\partial T}\right)_S = \frac{C_V P}{T(\partial P/\partial T)_V}$$

$$P = \frac{nRT}{V} \qquad \left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$$

$$\left(\frac{\partial U}{\partial T}\right)_S = \frac{C_V P}{nRT/V} = C_V = \frac{3}{2}nR$$

Name:

3. Solid sulfur occurs in two crystalline forms, rhombic and monoclinic. The solubility of rhombic sulfur in $CCl_{4(\ell)}$ is 0.262 molal at 298K. Given $\Delta_{r,m}G^{\ominus}$ for the reaction

$$S_{rhombic} \longrightarrow S_{monoclinic}$$

is 96.1 J mol^{-1} at 298 K, calculate the molal solubility of monoclinic sulfur in carbon tetrachloride at 298K. You should assume both solutions are sufficiently dilute that the solutes obey Henry's law.

Answer: Let $\mu^{\ominus}_{sulfur,\ell}$ be the standard chemical potential of sulfur in the liquid phase of a solution. Then

$$\mu^*_R(solid) = \mu^{\ominus}_{sulfur,\ell} + RT \ln \frac{m_R}{m_{\circ}}$$

$$\mu^*_M(solid) = \mu^{\ominus}_{sulfur,\ell} + RT \ln \frac{m_M}{m_{\circ}}$$
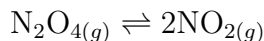
Subtracting

$$\mu^*_M - \mu^*_R = \Delta_{r,m}G^{\ominus} = RT \ln \frac{m_M}{m_R}$$

$$96.1 \text{ J mol}^{-1} = (8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K}) \ln \frac{m_M}{0.262 \text{ molal}}$$

$$m_M = 0.272 \text{ molal}$$

Name:

4. At a total pressure of 4.00 bar, it is found that the degree of dissociation α for the gas-phase process

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

is 0.140 at 298K and 0.200 at 308K. Assuming the standard enthalpy change for the reaction is temperature independent, calculate $\Delta_{r,m}H^{\ominus}$, $\Delta_{r,m}U$, $\Delta_{r,m}G^{\ominus}$ and $\Delta_{r,m}S^{\ominus}$ for the reaction at 298K.

Answer:

	$n_{N_2O_4}$	n_{NO_2}
initial	n	0
change	$-\alpha n$	$2\alpha n$
equilibrium	$n(1-\alpha)$	$2\alpha n$

$$n_{tot} = n(1+\alpha)$$

$$K = \frac{(P_{NO_2}/P^{\ominus})^2}{P_{N_2O_4}/P^{\ominus}} = \frac{4\alpha^2}{1-\alpha^2}\frac{P}{P^{\ominus}}$$

$$K(298) = 0.320 \qquad K(308) = 0.667$$

$$\ln\frac{K_2}{K_1} = \frac{\Delta_{r,m}H^{\ominus}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\frac{0.667}{0.320} = \frac{\Delta_{r,m}H^{\ominus}}{8.3144 \text{ J mol}^{-1}\text{K}^{-1}}\left(\frac{1}{298 \text{ K}} - \frac{1}{308 \text{ K}}\right) \qquad \Delta_{r,m}H^{\ominus} = 56000 \text{ J mol}^{-1}$$
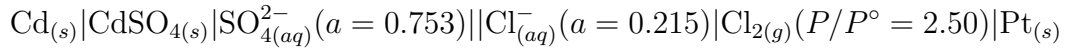
$$\Delta_{r,m}G^{\ominus} = -RT\ln K = -(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})\ln 0.323 = 2823 \text{ J mol}^{-1}$$

$$\Delta_{r,m}S^{\ominus} = \frac{\Delta_{r,m}H^{\ominus} - \Delta_{r,m}G^{\ominus}}{T} = 178 \text{ J K}^{-1}$$

$$\Delta_{r,m}U = \Delta_{r,m}H^{\ominus} - RT\Delta n_{gas} = 56000 \text{ J mol}^{-1} - (8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})(1) = 53500 \text{ J mol}^{-1}$$
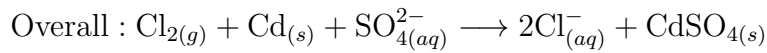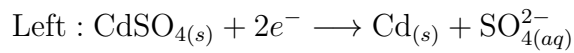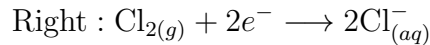
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5. At 298K the EMF of the cell

$$Cd_{(s)}|CdSO_{4(s)}|SO^{2-}_{4(aq)}(a = 0.753)||Cl^-_{(aq)}(a = 0.215)|Cl_{2(g)}(P/P^\circ = 2.50)|Pt_{(s)}$$

is 1.652 V. Given the half-cell potentials of the chlorine and cadmium sulfate electrodes to be respectively $E^\circ_{Cl^-/Cl_2/Pt} = 1.35827$ V and $E^\circ_{SO_4^{2-}/CdSO_4/Cd} = -0.246$ V, calculate the fugacity coefficient of the chlorine gas in the cell.

Answer:

$$\text{Right}: Cl_{2(g)} + 2e^- \longrightarrow 2Cl^-_{(aq)}$$

$$\text{Left}: \underline{CdSO_{4(s)} + 2e^- \longrightarrow Cd_{(s)} + SO^{2-}_{4(aq)}}$$

$$\text{Overall}: Cl_{2(g)} + Cd_{(s)} + SO^{2-}_{4(aq)} \longrightarrow 2Cl^-_{(aq)} + CdSO_{4(s)}$$

$$E^\ominus = E^\ominus_R - E^\ominus_L = 1.60427 \text{ V}$$

$$Q = \frac{(a_{Cl^-})^2}{a_{SO_4^{2-}} f_{Cl_2}/P^\ominus}$$

$$E = E^\ominus - \frac{RT}{nF} \ln Q$$

$$1.6524 \text{ V} = 1.60427 \text{ V} - \frac{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})}{2(96485 \text{ C mol}^{-1})} \ln \frac{(0.215)^2}{(0.753)f/P^\ominus}$$

$$f = 2.60 \text{ bar} = \gamma P = \gamma(2.50 \text{ bar}) \qquad \gamma = 1.04$$

Name:

6. The enthalpy of vaporization of rubbing alcohol (liquid isopropan-2-ol, $CH_3CHOHCH_3$) is $\Delta_{vap,m}H$= 44.0 kJ mol^{-1}, and the vapor pressure of rubbing alcohol is 5.79 $\times 10^{-2}$ bar at 296 K. A 10.00 L tank fitted with a frictionless piston contains excess liquid rubbing alcohol in equilibrium with its vapor, and the assembly is immersed in a heat bath at a fixed temperature of 308 K. The piston is compressed isothermally against a constant external pressure of 1.00 bar to a final volume of 5.00 L. Calculate $q, w, \Delta U, \Delta H, \Delta S$ and ΔG for the compression process.

Answer:

$$\ln \frac{P_{308}}{P_{296}} = \frac{\Delta_{vap,m}H}{R} \left(\frac{1}{296 \text{ K}} - \frac{1}{308 \text{ K}} \right)$$

$$\ln \frac{P_{308}}{5.79 \times 10^{-2} \text{ bar}} = \frac{44000 \text{ J mol}^{-1}}{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})} \left(\frac{1}{296 \text{ K}} - \frac{1}{308 \text{ K}} \right) \qquad P_{308} = 0.116 \text{ bar}$$

$$w = -P_{ext}\Delta V = -(1.00 \text{ bar})(5.00 \text{ L} - 10.0 \text{ L}) = 5.00 \text{ L bar} = 500 \text{ J}$$

$$\Delta n = \frac{P\Delta V}{RT} = \frac{(0.116 \text{ bar})(-5.00 \text{ L})}{(0.083144 \text{ L bar mol}^{-1}\text{K}^{-1})(308 \text{ K})} = -2.26 \times 10^{-2} \text{ mol}$$

$$\Delta H = (2.26 \times 10^{-2} \text{ mol})(-44000 \text{ J mol}^{-1}) = -994 \text{ J}$$

$$\Delta U = \Delta H - \Delta(PV) = \Delta H - RT\Delta n = -994 \text{ J} - (8.3144 \text{ J mol}^{-1}\text{K}^{-1})(308 \text{ K})(-2.26 \times 10^{-2} \text{ mol}) = -936 \text{ J}$$

$$q = \Delta U - w = -1436 \text{ J}$$

$$\Delta S = \frac{\Delta H}{T} = \frac{994 \text{ J}}{308 \text{ K}} = 3.24 \text{ J K}^{-1}$$

$$\Delta G = \Delta H - T\Delta S = 0$$

Name: