

Chemistry 431  
Final Exam  
Fall 2023  
Solutions

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

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

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

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

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

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

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

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

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

$$1 \text{ kg} = 1000. \text{ g}$$

$$1 \text{ L} = 10^3 \text{ cm}^3$$

$$10^2 \text{ cm} = 1 \text{ m}$$

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

$$T = t + 273.15$$

$$1 + x + x^2 + x^3 + \dots = 1/(1 - x) \quad |x| < 1$$

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

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Name:

1. A cylinder fitted with a frictionless piston initially contains 2.00 moles of an ideal diatomic gas at 298 K at an initial pressure of 4.25 bar. The gas undergoes an adiabatic compression against a constant external pressure of 7.00 bar until equilibrium is reached. Calculate  $\Delta U$ ,  $\Delta H$ ,  $\Delta S$ ,  $q$  and  $w$  for the process.

**Answer:**

$$q = 0$$

$$w = \Delta U = C_V \Delta T = -P_{ext} \Delta V$$

$$\frac{5}{2} nR(T_f - 298 \text{ K}) = -P_{ext} \left( \frac{nRT_f}{P_{ext}} - \frac{nR298 \text{ K}}{P_{init}} \right)$$

$$\frac{5}{2} T_f - 745 \text{ K} = -T_f + 491 \text{ K} \quad T_f = 353 \text{ K}$$

$$w = \Delta U = C_V \Delta T = \frac{5}{2} nR \Delta T = \frac{5}{2} (2.00 \text{ mol})(8.3144 \text{ J mol}^{-1} \text{K}^{-1})(353 \text{ K} - 298 \text{ K}) = 2286 \text{ J}$$

$$\Delta H = C_P \Delta T = \frac{7}{5} \Delta U = 3021 \text{ J}$$

$$\Delta S = nR \ln \frac{P_i}{P_f} + C_P \ln \frac{T_f}{T_i} = (2.00 \text{ mol})(8.3144 \text{ J mol}^{-1} \text{K}^{-1}) \left[ \ln \frac{4.25}{7.00} + \frac{7}{2} \ln \frac{353}{298} \right] = 1.56 \text{ J K}^{-1}$$

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Name:

2. For a van der Waals fluid that obeys the equation of state

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

with  $a$  and  $b$  numerical constants, derive an expression for  $\left(\frac{\partial P}{\partial T}\right)_U$  in terms of  $a, b, n, T, V$  and the constant volume heat capacity  $C_V$ .

**Answer:**

$$\begin{aligned} dP &= \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV \\ \left(\frac{\partial P}{\partial T}\right)_U &= \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_U \\ \left(\frac{\partial V}{\partial T}\right)_U \left(\frac{\partial T}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_T &= -1 \\ \left(\frac{\partial V}{\partial T}\right)_U &= -\frac{\left(\frac{\partial U}{\partial T}\right)_V}{\left(\frac{\partial U}{\partial V}\right)_T} = -\frac{C_V}{\left(\frac{\partial U}{\partial V}\right)_T} \\ dU &= TdS - PdV \\ \left(\frac{\partial U}{\partial V}\right)_V &= T \left(\frac{\partial S}{\partial V}\right)_T - P \\ dA &= -SdT - PdV \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \\ \left(\frac{\partial V}{\partial T}\right)_U &= -\frac{C_V}{T \left(\frac{\partial P}{\partial T}\right)_V - P} \\ \left(\frac{\partial P}{\partial T}\right)_U &= \left(\frac{\partial P}{\partial T}\right)_V - \frac{\left(\frac{\partial P}{\partial V}\right)_T C_V}{T \left(\frac{\partial P}{\partial T}\right)_V - P} \\ \left(\frac{\partial P}{\partial T}\right)_V &= \frac{nR}{V - nb} \quad \left(\frac{\partial P}{\partial V}\right)_T = -\frac{nRT}{(V - nb)^2} + \frac{an^2}{V^2} \\ \left(\frac{\partial P}{\partial T}\right)_U &= \frac{nR}{V - nb} - \frac{\left[-\frac{nRT}{(V - nb)^2} + \frac{an^2}{V^2}\right] C_V}{\frac{an^2}{V^2}} \end{aligned}$$

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Name:

3. The normal boiling point of methanol ( $\text{CH}_3\text{OH}$ ) is  $64.7^\circ\text{C}$ , and the vapor pressure of methanol is  $0.01302$  bar at  $20.0^\circ\text{C}$ . A cylinder fitted with a frictionless piston at  $50.0^\circ\text{C}$  contains sufficient liquid methanol that both liquid and vapor-phase methanol are present in all stages of the process that follows. The initial volume of the system is  $1.25$  L, and the piston expands isothermally against a constant external pressure of  $0.5$  times the vapor pressure of methanol at  $50.0^\circ\text{C}$  to a final volume of  $1.50$  L. Given the enthalpy of vaporization of methanol is  $35.21$   $\text{kJ mol}^{-1}$  and assuming the liquid volume of methanol is negligible compared to the vapor phase, calculate  $q$ ,  $w$ ,  $\Delta H$ ,  $\Delta U$ ,  $\Delta S$ ,  $\Delta G$  and  $\Delta A$  for the expansion.

**Answer:**

$$\ln \frac{P_2}{P_1} = \frac{\Delta_{\text{vap},m}H}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{P_{323}}{0.01302} = \frac{35210 \text{ J mol}^{-1}}{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})} \left( \frac{1}{293 \text{ K}} - \frac{1}{323 \text{ K}} \right) \quad P_{323} = 4.98 \times 10^{-2} \text{ bar}$$

$$w = -P_{\text{ext}}\Delta V = -(0.249 \times 10^{-2} \text{ bar})(1.50 \text{ L} - 1.25 \text{ L})(100 \text{ J L}^{-1}\text{bar}^{-1}) = -0.624 \text{ J}$$

$$\Delta n = \frac{P\Delta V}{RT} = \frac{(4.98 \times 10^{-2} \text{ bar})(0.25 \text{ L})}{(0.083144 \text{ L bar mol}^{-1}\text{K}^{-1})(323 \text{ K})} = 4.64 \times 10^{-4} \text{ mol}$$

$$\Delta H = (\Delta_{\text{vap},m}H)\Delta n = (4.64 \times 10^{-4} \text{ mol})(35210 \text{ J mol}^{-1}) = 16.3 \text{ J}$$

$$\Delta U = \Delta H - \Delta(PV) = \Delta H - P\Delta V = 16.3 \text{ J} - (4.98 \times 10^{-2} \text{ bar})(0.25 \text{ L})(100 \text{ J L}^{-1}\text{bar}^{-1}) = 15.1 \text{ J}$$

$$q = \Delta U - w = 15.1 \text{ J} - (-0.624 \text{ J}) = 15.7 \text{ J}$$

$$\Delta S = \frac{\Delta H}{T} = \frac{16.3 \text{ J}}{323 \text{ K}} = 5.05 \times 10^{-2} \text{ J K}^{-1}$$

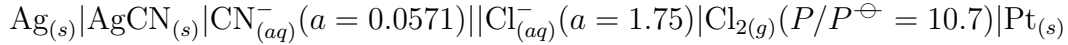
$$\Delta G = \Delta H - T\Delta S = 0$$

$$\Delta A = \Delta U - T\Delta S = 15.1 \text{ J} - (323 \text{ K})(5.05 \times 10^{-2} \text{ J K}^{-1}) = -1.21 \text{ J}$$

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Name:

4. At 298 K, the EMF of the electrochemical cell

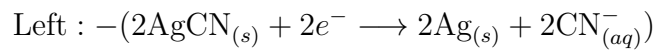
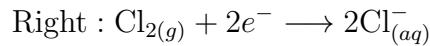


is  $E = 1.318$  volts. The standard half-cell potentials for the two electrodes of the cell are  $E^\ominus_{\text{Ag}/\text{AgCN}/\text{CN}^-} = -0.017$  V and  $E^\ominus_{\text{Cl}^-/\text{Cl}_2/\text{Pt}} = 1.35827$  V, and the chlorine gas obeys the equation of state

$$P = \frac{RT}{V_m - b}$$

where  $b$  represents the volume occupied by the chlorine molecules. Use the experimental data to determine the fugacity coefficient of the chlorine. Derive an expression for the fugacity coefficient from the equation of state, and determine the value of  $b$  implied by the electrochemical data.

**Answer:**



$$Q = \frac{a_{\text{Cl}^-}^2}{a_{\text{CN}^-}^2 \frac{P_{\text{Cl}_2}}{P^\ominus} \gamma}$$

$$E^\ominus = E^\ominus_{\text{Cl}^-/\text{Cl}_2/\text{Pt}} - E^\ominus_{\text{Ag}/\text{AgCN}/\text{CN}^-} = 1.35827 \text{ V} - (-0.017 \text{ V}) = 1.375 \text{ V}$$

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

$$1.318 \text{ V} = 1.375 \text{ V} - \frac{(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})}{2(96485 \text{ C mol}^{-1})} \ln \frac{1.75^2}{(0.0571)^2(10.7)\gamma} \quad \gamma = 1.04$$

$$z = \frac{PV_m}{RT} = 1 + \frac{Pb}{RT}$$

$$\gamma = \exp\left(\int_0^P \frac{z-1}{P} dP\right) = \exp\left(\frac{bP}{RT}\right)$$

$$\ln(1.04) = \frac{(10.7 \text{ bar})b}{(0.083144 \text{ L bar mol}^{-1}\text{K}^{-1})(298 \text{ K})} \quad b = 0.0908 \text{ L mol}^{-1}$$

Name:

5. At 298 K the vapor pressure of pure liquid benzene ( $C_6H_6$ ) is 0.126 bar and the vapor pressure of pure liquid toluene ( $C_6H_5CH_3$ ) is 0.131 bar. A mixture containing 10.0 g of benzene and 10.0 g of toluene is allowed to come to equilibrium with the vapor phase. Assuming toluene and benzene form an ideal solution obeying Raoult's Law, calculate 1) the mole fraction of benzene in the vapor phase of the mixture and 2) the change in the Gibbs free energy when 10.0 g of toluene and 10.0 g of benzene mix.

**Answer:**

$$n_B = \frac{10.0 \text{ g}}{78.0 \text{ g mol}^{-1}} = 0.128 \text{ mol} \quad n_T = \frac{10.0 \text{ g}}{92.0 \text{ g mol}^{-1}} = 0.109 \text{ mol}$$

$$\chi_B = \frac{0.128}{0.128 + 0.109} = 0.54 \quad \chi_T = 1 - \chi_B = 0.46$$

$$P_B = \chi_B P_B^* = (0.54)(0.126 \text{ bar}) = 0.0680 \text{ bar}$$

$$P_T = \chi_T P_T^* = (0.46)(0.131 \text{ bar}) = 0.0603 \text{ bar}$$

$$P_{tot} = P_B + P_T = 0.128 \text{ bar}$$

In the vapor phase

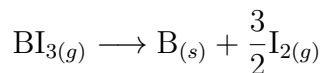
$$P_B = \chi_B P_{tot} \quad \chi_B = \frac{0.0680}{0.128} = 0.53 \quad \chi_T = 1 - \chi_B = 0.47$$

$$\begin{aligned} \Delta_{mix}G &= nRT[\chi_B \ln \chi_B + \chi_T \ln \chi_T] \\ &= ((0.128 \text{ mol} + 0.109 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(298 \text{ K})[0.54 \ln 0.54 + 0.46 \ln 0.46]) = -405 \text{ J} \end{aligned}$$

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Name:

6. When boron triiodide gas dissociates at a total pressure of 1.00 bar according to the reaction



it is found that the degree of dissociation  $\alpha$  is 0.0561 at 25.0°C and 0.228 at 50.0°C. Calculate  $\Delta_{r,m}G$  for the reaction at 35.0°C when the partial pressure of boron triiodide is 0.253 bar and the partial pressure of iodine gas is 1.36 bar. Predict whether the reaction proceeds to the right or left at the specified conditions.

**Answer:**

$n_{\text{BI}_3}$	$n_{\text{I}_2}$
$n_0$	0
$-\alpha n_0$	$3/2 \alpha n_0$
$n_0(1 - \alpha)$	$3/2 \alpha n_0$

$$n_{tot} = n_0(1 - \alpha) + \frac{3}{2}\alpha n_0 = n_0 \left(1 + \frac{\alpha}{2}\right)$$

$$K_P = \frac{\left(\left(\frac{3\alpha/2}{1 + \alpha/2}\right)(P/P^\ominus)\right)^{3/2}}{\left(\frac{1 - \alpha}{1 + \alpha/2}\right)(P/P^\ominus)}$$

$$K(298) = 0.0255 \quad K(323) = 0.245$$

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

$$\ln \frac{0.245}{0.0255} = \frac{\Delta_{r,m}H^\ominus}{R} \left(\frac{1}{298 \text{ K}} - \frac{1}{323 \text{ K}}\right) \quad \frac{\Delta_{r,m}H^\ominus}{R} = 8711 \text{ K}$$

$$\ln \frac{K(308)}{0.0255} = 8711 \text{ K} \left(\frac{1}{298 \text{ K}} - \frac{1}{308 \text{ K}}\right) \quad K(308) = 0.0659$$

$$\Delta_{r,m}G^\ominus = -RT \ln K = -(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(308 \text{ K}) \ln 0.0659 = 6964 \text{ J}$$

$$\Delta_{r,m}G = \Delta_{r,m}G^\ominus + RT \ln Q$$

$$= 6964 \text{ J} + (8.3144 \text{ J mol}^{-1}\text{K}^{-1})(308 \text{ K}) \ln \frac{1.36^{3/2}}{0.253} = 11665 \text{ J}$$

Spontaneous to left.

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Name:

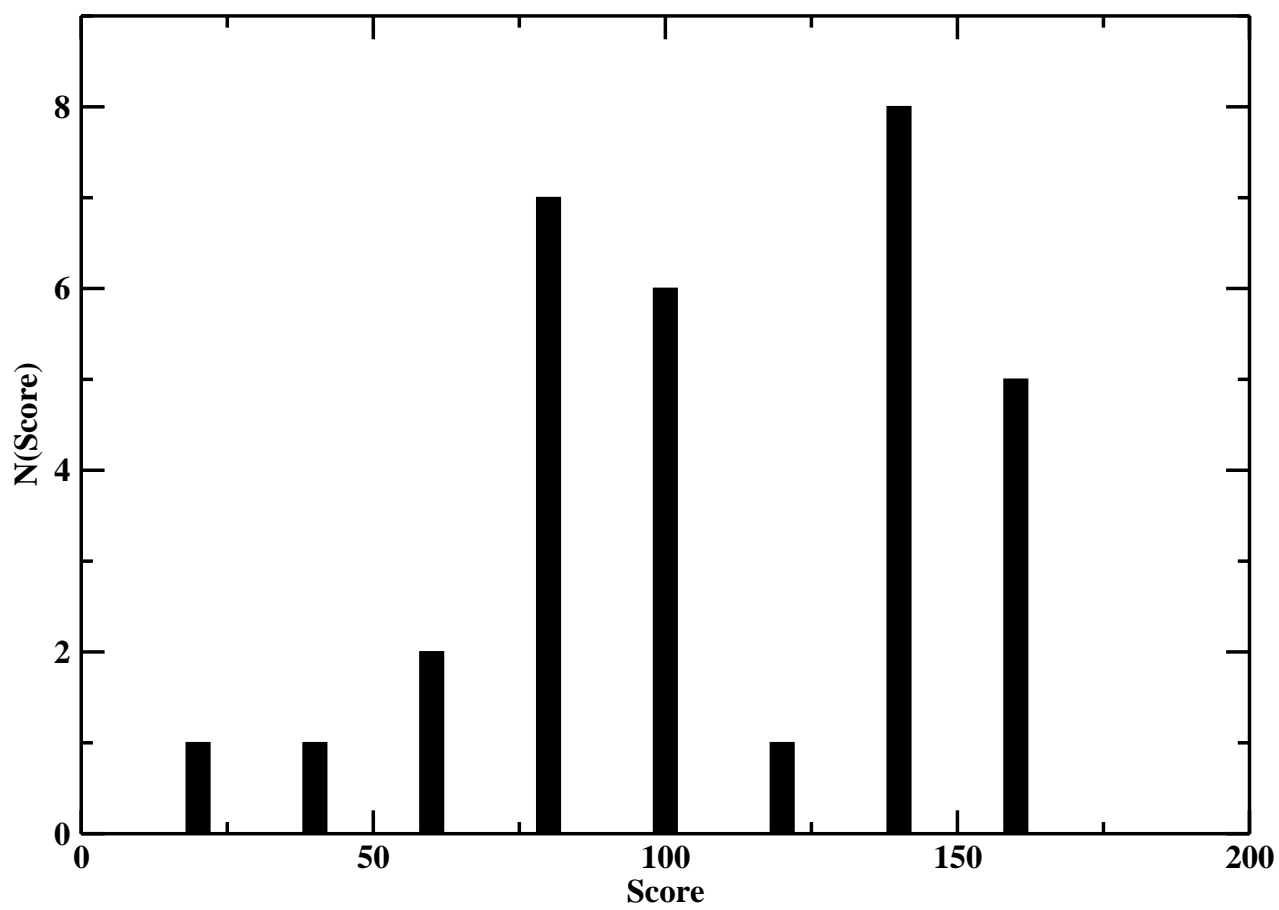


Figure 1: High = 179, Median = 116, Mean = 117