

1. Evaluate the following derivatives:

1a.  $\frac{d}{dx} \left[ \ln(4x^2 + 3x + 1) \right]$

Solution:

$$\begin{aligned} & \frac{d}{dx} \left[ \ln(4x^2 + 3x + 1) \right] \\ &= \frac{1}{(4x^2 + 3x + 1)} (8x + 3) \end{aligned}$$

1b.  $\frac{d}{dT} \left[ \frac{\Delta G}{RT} \right]$

Solution:

$$\begin{aligned} & \frac{d}{dT} \left[ \frac{\Delta G}{RT} \right] \\ &= \frac{d}{dT} \left[ \frac{(\Delta H - T\Delta S)}{RT} \right] \\ &= -\frac{\Delta H}{RT^2} + \frac{1}{RT} \frac{d\Delta H}{dT} - \frac{d\Delta S}{RdT} \end{aligned}$$

2. Evaluate the following integral

2a.  $\int \left[ -\frac{RT}{\bar{V}^2} \right] d\bar{V}$

Solution:

$$\begin{aligned} & \int \left[ -\frac{RT}{\bar{V}^2} \right] d\bar{V} \\ &= \frac{RT}{\bar{V}} + C \end{aligned}$$

Name \_\_\_\_\_

1. (7 Points) Consider a gas that is described by the following equation of state:

$$P = \frac{(nRT)}{V - nb} - \frac{n^2 a}{V^2}$$

where P is total pressure, T is the temperature, V is total volume of the container holding the gas, n is the number of moles of gas, and "a" and "b" are constants characteristic of the gas. R is the gas constant. For an expansion of n = 1 mole of this gas from volume = V<sub>1</sub> to volume = V<sub>2</sub> derive an expression for the maximum work obtainable from an isothermal expansion of this gas at temperature T.

Solution:

$$\begin{aligned} (work)_{\max} &= w_{rev} = - \int_{V_1}^{V_2} P dV \\ &= - \int_{V_1}^{V_2} \left( \frac{(nRT)}{V - nb} - \frac{n^2 a}{V^2} \right) dV \\ &= -nRT \ln \left( \frac{V_2 - nb}{V_1 - nb} \right) - n^2 a \left( \frac{1}{V_2} - \frac{1}{V_1} \right) \end{aligned}$$

2. (3 Points) The constant "a" and "b" for carbon dioxide are a = 3.658 bar L<sup>2</sup>/mol<sup>2</sup> and b = 0.0429 L/mol, respectively. At T = 273.15K, what is the numerical value of the maximum work done by the fluid in question 1 upon expansion from volume V<sub>1</sub> = 20L to V<sub>2</sub> = 40L. Would the maximum work for an ideal gas undergoing such an expansion be larger or smaller, and why?

Solution:

$$\begin{aligned} &= -nRT \ln \left( \frac{V_2 - nb}{V_1 - nb} \right) - n^2 a \left( \frac{1}{V_2} - \frac{1}{V_1} \right) \\ &= -(1mole) \left( \frac{8.314 J}{mole \cdot K} \right) (273.15K) \ln \left( \frac{40L - (1mole)(0.0429 \frac{L}{mole})}{20L - (1mole)(0.0429 \frac{L}{mole})} \right) - (1mole)^2 (3.658bar \frac{L^2}{mole^2}) \left( \frac{1}{40L} - \frac{1}{20L} \right) (0.986 \frac{atm}{bar}) (101.325 \frac{J}{L - atm}) \\ &= -(2270.9691) \ln \left( \frac{39.9571}{19.9571} \right) - (3.658) \left( \frac{-1}{40} \right) (0.986923) (101.325) \\ &= -(2270.9691J) (0.69422) + 9.145J \\ &= -1567.455J \end{aligned}$$

For an ideal gas, as we considered in class:

$$\begin{aligned} w_{rev}^{IG} &= -nRT \ln \left( \frac{V_2}{V_1} \right) = (-1)(8.314J/mol - K)(273.15K) \ln(40/20) \\ &= -1574.12J \end{aligned}$$

The ideal gas system provides more reversible work. The pressure for the ideal gas is higher for all volumes, thus giving rise to a larger area under the p-V curve for this process.

Name \_\_\_\_\_

1. (7 Points) Consider one mole of an ideal monatomic gas initially at the state point P = 2.0 bar and T = 273K. The gas undergoes a reversible process taking it to a final state point where P = 4.0 bar. The process is described by a path along which the following holds:  $\frac{P}{V} = \text{constant} = C$ .

Calculate  $\Delta U$ ,  $\Delta H$ ,  $q$ ,  $w$  for this process. Take the molar constant volume heat capacity (independent of temperature for this case) to be  $\bar{C}_V = 12.5 \frac{J}{mol \cdot K}$ .

Solution:

Since  $(P/V) = \text{constant}$ , we have:

$$\frac{P_1}{V_1} = \frac{P_2}{V_2}, \text{ thus, } T_2 = \frac{P_2 V_2}{R} = \frac{P_2^2}{CR}$$

We can find the constant C as:

$$C = \frac{P_1^2}{T_1 R} = \frac{4.0 \text{ bar}^2}{(273K)R}$$

Thus, T2 is:

$$T_2 = \frac{P_2 V_2}{R} = \frac{P_2^2}{\left(\frac{4.0 \text{ bar}^2}{(273K)R}\right)R} = \frac{16.0 \text{ bar}^2}{\left(\frac{4.0 \text{ bar}^2}{(273K)R}\right)R} = 1092K$$

Because the constant volume specific heat is temperature independent, we can write:

$$\Delta U = \bar{C}_V (T_2 - T_1) = (1 \text{ mol})(12.5 \text{ J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1})(1092K - 273K) = 10.2 \text{ kJ}$$

The work for this process, taken to be reversible **along the path described** is:

$$\begin{aligned} w &= -\int_{V_1}^{V_2} P dV = -\int_{V_1}^{V_2} C V dV = \frac{-C}{2} (V_2^2 - V_1^2) \\ &= \frac{-C}{2C^2} (P_2^2 - P_1^2) = \frac{-1}{2C} (P_2^2 - P_1^2) = \frac{-(273K)(R)(12 \text{ bar}^2)}{(2)(4 \text{ bar}^2)} = \frac{-(273K)(0.083145 \text{ bar} \cdot \text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(12 \text{ bar}^2)}{(2)(4 \text{ bar}^2)} \\ &= -3.4 \text{ kJ} \end{aligned}$$

The heat interaction for this process is:

$$q = \Delta U - w = 13.6 \text{ kJ}$$

And the enthalpy change is finally:

$$\begin{aligned}\Delta H &= \Delta U + nR\Delta T = 10.2 \text{ kJ} + (8.314 \text{ J/mol} \cdot \text{K})(819 \text{ K}) \\ &= 17.0 \text{ kJ}\end{aligned}$$

2. (1 Point) Consider a generic fluid. In the limit,  $pressure \rightarrow 0$  which of the following holds; more than one answer is possible (write the number of the item explicitly):

1.  $\mu_{j-T} \rightarrow 0$
2.  $dH = C_V dT$
3.  $dU = dq$
4.  $dU = C_V dT - C_V \eta_j dV$
5.  $pV = nRT$
6.  $T_{\text{inversion}} = 298 \text{ K}$

**Solution:**

1,4,5

3. (1 Point) For a mixture of ideal gases, A, B, and C, with  $n_A$  moles of A,  $n_B$  moles of B, and  $n_C$  moles of C, contained in a volume  $V$  what are the partial pressures of each gas and what is the total pressure?

**Solution:**

$$\begin{aligned}P_{\text{Total}} &= (P_A + P_B + P_C) \\ P_A &= \frac{n_A RT}{V}; P_B = \frac{n_B RT}{V}; P_C = \frac{n_C RT}{V}\end{aligned}$$

**4. (1 Point)**

Consider the following two processes:

1. Isothermal, reversible expansion of ideal gas from  $(P_1, V_1, T_1)$  to  $(P_2, V_2, T_1)$
2. Adiabatic, reversible expansion of ideal gas from  $(P_1, V_1, T_1)$  to  $(P_3, V_2, T_2)$

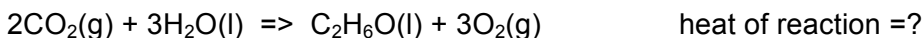
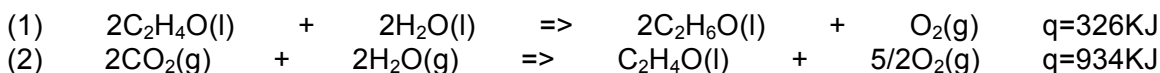
Is the following True or False?

$$T_1 < T_2 \text{ and } P_3 > P_2$$

**Solution:**

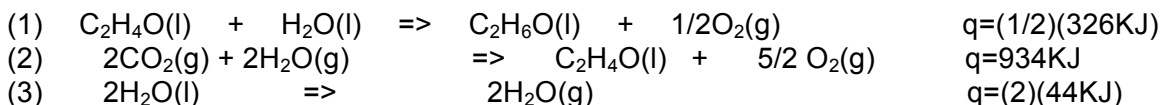
False

1. (2 Points) Use the thermochemical equations shown below to determine the enthalpy for the final reaction:



Solution:

The desired reaction is obtained as a combination of one-half of reaction 1 and reaction 2. The only twist is that a conversion between liquid to gaseous water is needed to complete the stoichiometry. The necessary information is obtained from the data tables provided in the equations handbook.



The total reaction enthalpy is thus the sum of the three values on the right (including the multiplicative factors to take into account proper stoichiometry):

Enthalpy (heat) of reaction = 1185.0 kJ

2. (8 Points) In an experiment to determine the caloric value of food, a sample of foodstuffs is burned (oxidized) in an oxygen atmosphere. The temperature of the calorimeter rose by 2.89 Celsius. When a current of 1.27 Amperes from a 12.5 Volt source flowed through the same calorimeter for 157 seconds, the temperature rose by 3.88 Celsius. What is the heat of combustion for the food? The energy associated as heat for a current of "I" Amperes due to a voltage "V" for "t" seconds is  $E = IVt$ . Keep in mind that 1 (Volt)(Ampere) = 1 Joule/second.

Solution:

Since we don't know the calorimeter heat capacity, we can use the result of the second experiment involving the heating of the calorimeter using a current source. The heat introduced by the current is given by:

$$\begin{aligned} q &= IVt = (1.27\text{A})(12.5\text{V})(157\text{s}) \\ &= 2492.375\text{J} \end{aligned}$$

The heat capacity is then related to the ratio heat to temperature change:

$$\begin{aligned} C_p &= q/\Delta T = (2492.375\text{J})/(3.88 \text{ }^\circ\text{C}) \\ &= 642.365\text{J}/^\circ\text{C} \end{aligned}$$

Returning to the original experiment to determine the heat of reaction for the combustion of the foodstuffs, we obtain the heat (enthalpy) of reaction straightforwardly as:

$$q = \Delta H_{\text{combustion}} = C_p \Delta T = (642.365 \text{ J / } ^\circ\text{C})(2.89^\circ\text{C}) \\ = 1856.4 \text{ J}$$

1. (3 Points) What is the efficiency of a Carnot cycle operating between 170°C and 620°C.

$$\epsilon_{Carnot} = 1 - \frac{T_{cold}}{T_{hot}} = 1 - \frac{(170 + 273.15)}{(620 + 273.15)} = .504$$

2. (8 Points) In Southern California, home of sun, surf, and great times, the Fall season brings the chance of Santa Ana winds. This meteorological event involves extremely rapid compression of large amounts of air as the winds blow from the higher elevations (the coastal mountains) to the ocean. Coupled with the drying of vegetation throughout the summer months, this event sets up the chance for serious wildfires (attached is a satellite photo from outer space of the 2005 wildfires in San Diego and environs). Based on your knowledge of thermodynamics, how would you determine the temperature of the air as it reaches sea-level after starting from an elevation in the mountains where the pressure,  $P_1$ , and temperature,  $T_1$ , are known; you can call the final sea-level temperature  $T_2$  and the pressure  $P_2$ . Recall that the compression occurs extremely rapidly.

Solution:

This is easily solved by considering an adiabatic, reversible compression of an ideal gas (assuming the mixture of gases we consider our atmosphere to be an ideal gas at low pressures up to 1 atmosphere). We have seen in class that for such a reversible, adiabatic compression of an ideal gas, the relation that holds is:



$$PV^\gamma = \text{constant}$$

$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

$$P_1^{1-\gamma} (RT_1)^\gamma = P_2^{1-\gamma} (RT_2)^\gamma$$

Thus, knowing all constants for an ideal gas, we can estimate  $T_2$ , the sea-level temperature, based on the pressure in the mountains, the pressure at sea level, and the temperature in the mountains.



1. **(10 Points)** One mole of an ideal gas at 300 K is reversibly and isothermally compressed from a volume of 25.0 L to a volume of 10.0 L. The external temperature bath remains at 300 K during the process. Calculate  $\Delta S_{system}$ ,  $\Delta S_{surroundings}$ , and  $\Delta S_{Total}$  for this process.

Solution:

$$\Delta U = 0$$

$$dq = -dw_{rev} = pdV = nRTd(\ln V)$$

$$q = -w_{rev} = RT \ln \left( \frac{V_{final}}{V_{initial}} \right)$$

$$\Delta S_{system} = \frac{q}{T} = R \ln \left( \frac{V_{final}}{V_{initial}} \right) = -7.62 J K^{-1}$$

Since the process is reversible, the total entropy change is zero, and the entropy change for the surroundings is the negative of the entropy change of the system,  $\Delta S_{surroundings} = +7.62 J/K$ .

1. **(5 Points)** One mole of H<sub>2</sub>O (liquid) is super-cooled to -2.25 Celsius at 1 bar pressure. The equilibrium freezing temperature at this pressure is 0.0 Celsius. The transformation H<sub>2</sub>O (liquid) → H<sub>2</sub>O (solid) is suddenly observed to occur. Show that the transformation (i.e., freezing) is spontaneous at this state point. Consider the surroundings to be at constant temperature of -2.25 Celsius. The following information may be useful:

$$C_p(\text{H}_2\text{O, liquid}) = 75.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_p(\text{H}_2\text{O, solid}) = 37.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H_{\text{fusion}} = 6.008 \text{ kJ mol}^{-1} \text{ at } 0.0 \text{ Celsius}$$

**Solution:**

As discussed in the class notes for October 24, 2011, the process appears irreversible (spontaneous) since water at -2.25 Celsius is freezing to solid (this is supercooled water). Thus, we need to construct a reversible path to compute the entropy change of the system. The entropy change of the surroundings is determined by the enthalpy of reaction (enthalpy of freezing) at the temperature of the surroundings, T=-2.25 Celsius.

For the Entropy change of the water (our system), we use the reversible path: H<sub>2</sub>O(liquid, -2.25 Celsius) → H<sub>2</sub>O(liquid, 0.0 Celsius) → H<sub>2</sub>O(solid, 0.0 Celsius) → H<sub>2</sub>O(solid, -2.25 Celsius). The entropy change, at constant pressure, for this reversible transformation is:

$$\begin{aligned} \Delta S &= nC_{P,molar,liquid}^o \ln\left(\frac{273.15K}{270.90K}\right) - n \frac{\Delta H_{\text{fusion}}}{273.15K} + nC_{P,molar,solid}^o \ln\left(\frac{270.90K}{273.15K}\right) \\ &= -21.7 \text{ J K}^{-1} \end{aligned}$$

To calculate the entropy change of the surroundings, we compute the enthalpy of reaction at -2.25 Celsius and then divide the negative of that number by the temperature of the surroundings:

$$\begin{aligned}
\Delta H_R^o &= H_{product} - H_{reactant} \\
&= \sum_{product\ i} \nu_i (\Delta H_{f, product\ i}^o) - \sum_{reactant\ j} \nu_j (\Delta H_{f, reactant\ j}^o) \\
\frac{d(\Delta H_R^o)}{dT} &= \frac{d \left[ \sum_{product\ i} \nu_i (\Delta H_{f, product\ i}^o) - \sum_{reactant\ j} \nu_j (\Delta H_{f, reactant\ j}^o) \right]}{dT} \\
&= \left[ \sum_{product\ i} \nu_i \frac{d(\Delta H_{f, product\ i}^o)}{dT} - \sum_{reactant\ j} \nu_j \frac{d(\Delta H_{f, reactant\ j}^o)}{dT} \right] \\
&= \left[ \sum_{product\ i} \nu_i C_{P, molar, product\ i}^o - \sum_{reactant\ j} \nu_j C_{P, molar, reactant\ j}^o \right] \\
d(\Delta H_R^o) &= \left[ \sum_{product\ i} \nu_i C_{P, molar, product\ i}^o - \sum_{reactant\ j} \nu_j C_{P, molar, reactant\ j}^o \right] dT \\
\Delta H_R^o(T_2) &= \Delta H_R^o(T_1) + \int_{T_1}^{T_2} \left[ \sum_{product\ i} \nu_i C_{P, molar, product\ i}^o - \sum_{reactant\ j} \nu_j C_{P, molar, reactant\ j}^o \right] dT \\
\Delta H_R^o(270.9K) &= \Delta H_R^o(273.15K) + \int_{273.15K}^{270.9K} ((\nu_{water, solid} C_{P, molar, water, solid}^o) - (\nu_{water, liquid} C_{P, molar, water, liquid}^o)) dT \\
&= -6008\text{ J} + \int_{273.15K}^{270.9K} ((1)(37.7\text{ J K}^{-1}\text{ mol}^{-1}) - (1)(73.15\text{ J K}^{-1}\text{ mol}^{-1})) dT \\
&= -6008\text{ J} - (35.45\text{ J K}^{-1})(-2.25K) = -5928\text{ J}
\end{aligned}$$

The entropy change of the surroundings is:

$$\Delta S_{surroundings}^o(270.9K) = \frac{-\Delta H_R^o(270.9K)}{T_{surroundings}} = \frac{5928\text{ J}}{270.9K} = 21.9\text{ J K}^{-1}$$

The total change is:

$$\begin{aligned}
\Delta S_{total}^o(270.9K) &= \Delta S_{system}^o(270.9K) + \Delta S_{surroundings}^o(270.9K) = -21.7\text{ J K}^{-1} + 21.9\text{ J K}^{-1} \\
&= 0.2\text{ J K}^{-1} > 0
\end{aligned}$$

This is just marginally spontaneous as we are fairly close to the equilibrium freezing temperature at this pressure.

2. (5 Points) Under anaerobic conditions, glucose is broken down in muscle tissue to form lactic acid according to the reaction:



Thermochemical data for 298K are as follow:

	$\Delta H_f^\circ (kJ mol^{-1})$	$C_{p,molar}^\circ (J K^{-1} mol^{-1})$	$S_{molar}^\circ (J K^{-1} mol^{-1})$
$C_6H_{12}O_6$	-1273.1	219.2	209.2
$CH_3CHOHCOOH$	-673.6	127.6	192.1

Calculate  $\Delta S$  for the system (taken to be the reaction components), the surroundings, and the universe at T=310K. State any assumptions you invoke in your solution.

**Solution:**

We will assume that the heat capacities as given are constant in the temperature range we are interested in. First consider the standard entropy and enthalpy of reaction at 298K.

$$\Delta S_R^\circ = (2 \text{ moles lactic acid})(192.1 J K^{-1} mol^{-1}) - (1 \text{ mole glucose})(209.2 J K^{-1} mol^{-1}) = 175.0 J K^{-1}$$

$$\Delta H_R^\circ = (2 \text{ moles lactic acid})(-673.6 kJ mol^{-1}) + (1 \text{ mole glucose})(1273 kJ mol^{-1}) = -74.2 kJ mol^{-1}$$

To consider effects of temperature change from 298K to 310K on entropy and enthalpy, we use familiar expressions for the constant pressure temperature dependence of these state functions:

$$\begin{aligned}
\Delta H_R^o &= H_{product} - H_{reactant} \\
&= \sum_{product\ i} \nu_i (\Delta H_{f, product\ i}^o) - \sum_{reactant\ j} \nu_j (\Delta H_{f, reactant\ j}^o) \\
\frac{d(\Delta H_R^o)}{dT} &= \frac{d \left[ \sum_{product\ i} \nu_i (\Delta H_{f, product\ i}^o) - \sum_{reactant\ j} \nu_j (\Delta H_{f, reactant\ j}^o) \right]}{dT} \\
&= \left[ \sum_{product\ i} \nu_i \frac{d(\Delta H_{f, product\ i}^o)}{dT} - \sum_{reactant\ j} \nu_j \frac{d(\Delta H_{f, reactant\ j}^o)}{dT} \right] \\
&= \left[ \sum_{product\ i} \nu_i C_{P, molar, product\ i}^o - \sum_{reactant\ j} \nu_j C_{P, molar, reactant\ j}^o \right] \\
d(\Delta H_R^o) &= \left[ \sum_{product\ i} \nu_i C_{P, molar, product\ i}^o - \sum_{reactant\ j} \nu_j C_{P, molar, reactant\ j}^o \right] dT \\
\Delta H_R^o(T_2) &= \Delta H_R^o(T_1) + \int_{T_1}^{T_2} \left[ \sum_{product\ i} \nu_i C_{P, molar, product\ i}^o - \sum_{reactant\ j} \nu_j C_{P, molar, reactant\ j}^o \right] dT \\
\Delta H_R^o(310K) &= \Delta H_R^o(298K) + \int_{298K}^{310K} ((\nu_{lactic\ acid} C_{P, molar, lactic\ acid}^o) - (\nu_{glucose} C_{P, molar, glucose}^o)) dT \\
&= -74.1\text{ kJ} + \int_{298K}^{310K} ((2)(127.6\text{ J K}^{-1}\text{ mol}^{-1}) - (1)(219.2\text{ J K}^{-1}\text{ mol}^{-1})) dT \\
&= -74.1\text{ kJ} + (0.036\text{ kJ K}^{-1})(12K) = -73.7\text{ kJ}
\end{aligned}$$

Similarly for the reaction entropy at 310K, we have:

$$\begin{aligned}
\Delta S_R^o &= S_{product} - S_{reactant} \\
&= \sum_{product\ i} \nu_i (\Delta S_{f, product\ i}^o) - \sum_{reactant\ j} \nu_j (\Delta S_{f, reactant\ j}^o) \\
\frac{d(\Delta S_R^o)}{dT} &= \frac{d \left[ \sum_{product\ i} \nu_i (\Delta S_{f, product\ i}^o) - \sum_{reactant\ j} \nu_j (\Delta S_{f, reactant\ j}^o) \right]}{dT} \\
&= \left[ \sum_{product\ i} \nu_i \frac{d(\Delta S_{f, product\ i}^o)}{dT} - \sum_{reactant\ j} \nu_j \frac{d(\Delta S_{f, reactant\ j}^o)}{dT} \right] \\
&= \left[ \sum_{product\ i} \nu_i \frac{C_{P, molar, product\ i}^o}{T} - \sum_{reactant\ j} \nu_j \frac{C_{P, molar, reactant\ j}^o}{T} \right] \\
d(\Delta S_R^o) &= \left[ \sum_{product\ i} \nu_i \frac{C_{P, molar, product\ i}^o}{T} - \sum_{reactant\ j} \nu_j \frac{C_{P, molar, reactant\ j}^o}{T} \right] dT \\
\Delta S_R^o(310K) &= \Delta S_R^o(298K) + \int_{298K}^{310K} ((\nu_{lactic\ acid} C_{P, molar, lactic\ acid}^o) - (\nu_{glucose} C_{P, molar, glucose}^o)) d(\ln T) \\
&= -74.1\text{ kJ} + \int_{298K}^{310K} ((2)(127.6\text{ J K}^{-1}\text{ mol}^{-1}) - (1)(219.2\text{ J K}^{-1}\text{ mol}^{-1})) d(\ln T) \\
&= 175.0\text{ J K}^{-1} + (36.0\text{ J K}^{-1}) \ln\left(\frac{310K}{298K}\right) = 176.4\text{ J K}^{-1}
\end{aligned}$$

We now compute the entropy change of the surroundings at T=310K using the enthalpy of reaction at 310K.

$$\Delta S_{surroundings}^o(310K) = \frac{-\Delta H_R^o(310K)}{T_{surroundings}} = \frac{73.7\text{ kJ}}{310K} = 238\text{ J K}^{-1}$$

Finally, we compute the total entropy change as :

$$\begin{aligned}
\Delta S_{total}^o(310K) &= \Delta S_{system}^o(310K) + \Delta S_{surroundings}^o(310K) = 176.4\text{ J K}^{-1} + 238\text{ J K}^{-1} \\
&= 414\text{ J K}^{-1}
\end{aligned}$$

1. (**5 Points**) Based on your knowledge of thermodynamics, demonstrate that the internal energy for an ideal gas is only temperature dependent.

Solution:

If we consider the internal energy in a general sense to depend on temperature,  $T$ , and volume,  $V$ , then the total differential of the internal energy in the most general case is:

$$dU(T,V) = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

By definition, the temperature partial derivative is the constant volume heat capacity, which in general can be treated as temperature dependent.

$$dU(T,V) = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

The trick is to determine what the second partial derivative is. We can start with the combined First and Second Laws to write the fundamental equation as:

$$dU(S,V) = TdS - pdV$$

Taking the partial derivative of both sides with respect to volume at constant temperature, we obtain:

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

The entropy partial derivative is determined from a Maxwell Relation,

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

Thus,

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

For an ideal gas:

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

giving for the final relation for  $dU(T,V)$  of an **ideal gas**:

$$dU(T,V) = C_v dT + \left[ \frac{nRT}{V} - p \right] dV$$

$$dU(T,V) = C_v dT + 0$$

$$dU(T) = C_v dT$$

2 (3 Points) Calculate the change in Helmholtz Free Energy, A for the isothermal compression of 1.25 mol of an ideal gas at 298K from an initial volume of 25.0 L to a final volume of 14.5 L. Does it matter whether the path is reversible or irreversible?

$$dA(T,V) = -pdV - SdT$$

At constant temperature, the second term vanishes. For ideal gas, the EOS is  $pV=nRT$ , thus giving:

$$\begin{aligned} dA(T,V) &= -nRTd(\ln V) = -nRT \ln \left( \frac{V_2}{V_1} \right) \\ &= -(1.25 \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K}) \left( \ln \left( \frac{14.5 \text{ L}}{25.0 \text{ L}} \right) \right) \\ &= 1.69 \times 10^3 \text{ J} \end{aligned}$$

The value does not change whether the process is reversible or irreversible (A is a state function).

3 (2 Points) Fill in the blank:

- G reaches an extremum at equilibrium under conditions of constant \_\_\_T\_\_\_ and \_\_\_P\_\_\_ for a single component system and with no non-expansion work.
- A reaches an extremum at equilibrium under conditions of constant \_\_\_T\_\_\_ and \_\_\_V\_\_\_ for a single component system and with no non-expansion work.
- U reaches an extremum at equilibrium under conditions of constant \_\_\_S\_\_\_ and \_\_\_V\_\_\_ for a single component system and with no non-expansion work.
- S reaches an extremum at equilibrium under conditions of constant \_\_\_U\_\_\_ and \_\_\_V\_\_\_ for a single component system and with no non-expansion work.
- H reaches an extremum at equilibrium under conditions of constant \_\_\_S\_\_\_ and \_\_\_P\_\_\_ for a single component system and with no non-expansion work.



**1. (10 Points)** In this problem you will deal with vapor-liquid (2-phase) equilibrium of a binary (2-component) system. Consider the system acetonitrile(1)/nitromethane(2) to conform to ideal solution and ideal vapor behavior. The temperature dependence of the saturation (vapor) pressures of the two species is given by:

$$\ln P_1^{saturation} = 14.2724 - \frac{2945.47}{t + 224.0}$$
$$\ln P_2^{saturation} = 14.2043 - \frac{2972.64}{t + 209.0}$$

where pressure is in units of KPa (kilopascal) and temperature in the above relations is in degrees Celsius

**A.** For a liquid composition of  $x_1=0.6$ , what are the total pressure and the composition ( $y_1$  and  $y_2$ ) of the vapor phase at a temperature of 75 Celsius?

Solution:

The saturation (vapor) pressures for the system are determined from the given relations for 75 Celsius:

$$\ln P_1^{saturation} = 14.2724 - \frac{2945.47}{(75) + 224.0} = 83.21kPa$$
$$\ln P_2^{saturation} = 14.2043 - \frac{2972.64}{(75) + 209.0} = 41.98kPa$$

We now apply the equilibrium criteria of chemical potential equality for species in ideal solution and vapor phases (Raoult's Law) to determine the total pressure:

$$P^{Total} = P_1 + P_2 = y_1 P^{Total} + y_2 P^{Total} = x_1 P_1^{saturation} + x_2 P_2^{saturation} = x_1 P_1^{saturation} + (1 - x_1) P_2^{saturation}$$
$$= 0.6(83.21kPa) + 0.4(41.98kPa) = 66.72kPa$$

Vapor phase compositions are then:

$$y_1 = \frac{x_1 P_1^{saturation}}{P^{Total}} = \frac{(0.6)(83.21kPa)}{(66.72kPa)} = 0.7483$$
$$y_2 = 1 - y_1 = 0.2517$$

**B.** What are the saturation temperatures for each fluid at a pressure of  $P = 70kPa$ ?

Solution:

The saturation temperatures for this system at the given pressure are determined from the given relations for the temperature dependence of pure species saturation pressures:

$$t_1^{saturation} = \left( \frac{2945.47}{14.2724 - \ln P_1^{saturation}} \right) - 224.0 = 69.84C$$

$$t_2^{saturation} = \left( \frac{2972.64}{14.2043 - \ln P_2^{saturation}} \right) - 209.0 = 89.58C$$

1. (5 Points) For the chemical compound  $C_6H_5CHO$ , we are given the following information. What is the equilibrium vapor pressure of the pure material at 100 Celsius?

Pressure (atm)	Temperature(C)
1	179
45.9	422
?	100

Solution:

This is a simple application of the Clausius-Clapeyron relation (keeping in mind the assumptions built into its derivation). We are given data such that we can determine the enthalpy of vaporization of the fluid, which we will take as a constant value over the temperature interval considered in this problem

First we determine the vaporization enthalpy using the first two state points:

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

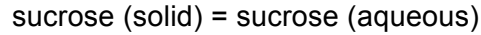
$$\Delta H = \frac{R \ln\left(\frac{P_2}{P_1}\right)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} = \frac{(8.314 J mol^{-1} K^{-1}) \ln\left(\frac{45.9 atm}{1 atm}\right)}{\left(\frac{1}{(273.15 + 179.0)} - \frac{1}{(273.15 + 422)}\right)} = 41.2 kJ mol^{-1}$$

Now we can pick one of the first two state points in conjunction with the 100 Celsius state point to estimate the vapor pressure at 100 Celsius.

$$\ln\left(\frac{P_2}{1 atm}\right) = \frac{41200 J mol^{-1}}{(8.314 J mol^{-1} K^{-1})} \left(\frac{1}{(273.15 + 179)} - \frac{1}{(273.15 + 100)}\right)$$

$$P_2 = 0.0981 atm$$

2. (5 Points) Consider the following simple transformation of hydrating sucrose at 25 Celsius:



A. Calculate the equilibrium constant based on your knowledge of thermodynamics.

Solution:

The Gibbs free energies for this reaction are from Table 7.7 in the Equations Handbook.

$$\begin{aligned} -RT \ln K_a &= \Delta G_{rxn}^{\circ} = \Delta G_{f, \text{sucrose}(aq)}^{\circ} - \Delta G_{f, \text{sucrose}(solid)}^{\circ} \\ -RT \ln K_a &= -1551.8 \frac{\text{kJ}}{\text{mol}} - \left( -1544.7 \frac{\text{kJ}}{\text{mol}} \right) = -7.1 \frac{\text{kJ}}{\text{mol}} \\ K_a &= \exp \left( \frac{7100 \frac{\text{J}}{\text{mol}}}{\left( 8.3144 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) (298.15 \text{K})} \right) = 17.5 \end{aligned}$$

B. Estimate the solubility (in molality units) of sucrose in water. State your assumptions and/or any other approximations you invoke.

Solution:

Using the value of the equilibrium constant computed above, we assume an ideal solution with the solute activity given by a Henry's Law activity model. We also consider the standard concentration to be 1 molal.

$$\begin{aligned} K_a &= \frac{a_{\text{sucrose}(aq)}}{a_{\text{sucrose}(solid)}} = \frac{a_{\text{sucrose}(aq)}}{1} = a_{\text{sucrose}(aq)} \\ &= \gamma_m \frac{m}{m^{\circ}} = \gamma_m m \approx (1)(m) = 17.5 \text{ molal} \end{aligned}$$

C. Experiments measure the concentration of sucrose at 25 Celsius to be 6.197 molal. What is your interpretation based on the results of parts A and B.

Solution:

The above results indicate that the assumption of ideality is not totally correct. To assess the extent of inadequacy, we can compute a ratio of approximate to experimental activity coefficients as:

$$\begin{aligned} K_a &= (\gamma_m m)^{\text{approximate}} = (\gamma_m m)^{\text{experimental}} \\ \frac{\gamma_m^{\text{experimental}}}{\gamma_m^{\text{approximate}}} &= \frac{m^{\text{approximate}}}{m^{\text{experimental}}} = \frac{17.5 \text{ molal}}{6.197 \text{ molal}} = 2.82 \end{aligned}$$

The deviation from ideality is significant due to the anticipated interactions between water and a polar, hydrogen-bonding solute such as sucrose.