

Answer each question in the space provided; use back of page if extra space is needed. Answer questions so the grader can READILY understand your work; only work on the exam sheet will be considered. Write answers, where appropriate, with reasonable numbers of significant figures. You may use **only** the "Student Handbook," a calculator, and a straight edge.

1. (20 Points) Calculate  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta H$  if 1.0 mole of an ideal gas with  $C_{V,m} = \frac{3}{2}R$  undergoes a reversible adiabatic expansion from an initial volume  $V_i = 5.25 \text{ m}^3$  to a final volume  $V_f = 25.5 \text{ m}^3$ . The initial temperature is 300K. Recall that for an ideal gas  $C_{P,m} = C_{V,m} + R$

$$dU = \delta q_{rev} + \delta w_{rev}$$

$$\delta q_{rev} = 0 \quad (\text{adiabatic})$$

$$\int_{T_i}^{T_f} C_{V,m} dT = - \int_{V_i}^{V_f} p dV = -RT \int_{V_i}^{V_f} d(\ln V)$$

$$\int_{T_i}^{T_f} C_{V,m} d(\ln T) = -R \int_{V_i}^{V_f} d(\ln V)$$

$$\frac{T_f}{T_i} = \left(\frac{V_f}{V_i}\right)^{1-\gamma} = \left(\frac{25.5L}{5.25L}\right)^{1-\frac{5}{3}} = 0.349$$

$$T_f = 105K$$

$$\Delta U = w_{rev} = C_{V,m}(T_f - T_i) = \frac{3}{2}R(105K - 300K) = \frac{3}{2}(8.314J/mol\ K)(105K - 300K) = -2.43 \times 10^3 J$$

$$\Delta H = C_{P,m}(T_f - T_i) = \frac{5}{2}R(105K - 300K) = -4.05 \times 10^3 J$$

**DO NOT WRITE  
IN THIS SPACE**

p. 1 \_\_\_\_\_/20

p. 2 \_\_\_\_\_/20

p. 3 \_\_\_\_\_/20

p. 4 \_\_\_\_\_/20

p. 5 \_\_\_\_\_/20

=====

p. 6 \_\_\_\_\_/10  
(Extra credit)

=====

TOTAL PTS

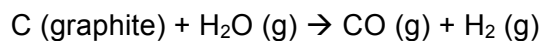
/100

NAME: \_\_\_\_\_

2. (20 Points) Complete the sentence in the left column using the answers provided in the right column. Where requested, explicitly write out True or False so as to avoid ambiguity.

<p>1. The reversible work needed to compress a gas is <u>H</u> that needed in an irreversible process affecting the same change.</p>	<p>a. equal to</p>
<p>2. An extensive thermodynamic property is independent of the amount of substance or system size. (True or False?) <u>FALSE</u></p>	<p>b. amount</p>
<p>3. The Joule-Thomson process is an <u>F</u> process.</p>	<p>c. volume, and pressure.</p>
<p>4. The Second Law of Thermodynamics allows us to formulate bounds on the amount of internal energy that can be converted to work. (True or False) <u>FALSE</u></p>	<p>d. isoenergetic</p>
<p>5. The internal energy of an ideal gas depends on temperature <u>G</u>.</p>	<p>e. greater than</p>
<p>6. We can write the standard enthalpy of reaction in a general form as:</p> $\Delta H_{reaction}^0(T) = \sum_{products,i} \nu_i \Delta H_{f,i}^0 - \sum_{react,j} \nu_j \Delta H_{f,j}^0$	<p>f. isenthalpic</p>
<p>because enthalpy has the quality of being a(n) <u>I (state function)</u>.</p>	<p>g. only h. less than i. state function j. inexact integral k. natural variable</p>

NAME: \_\_\_\_\_

**3. (20 Points)** Consider the following reaction:

The standard enthalpy of reaction at  $T=298.15\text{K}$  is  $\Delta H_{T=298.15}^0 = 131.28 \frac{\text{kJ}}{\text{mol}}$ . What is the standard enthalpy of reaction at  $125^\circ\text{C}$ ? Assume constant molar heat capacities.

$$\Delta H_{\text{reaction}}^\circ(T = 398.15\text{K}) = \Delta H_{\text{reaction}}^\circ(T = 298.15\text{K}) + \int_{T=298.15\text{K}}^{T=398.15\text{K}} \Delta C_{P,\text{rxn}} dT$$

$$\Delta C_{P,\text{rxn}} = \sum_i \nu_i C_{P,i}^\circ = (1)\left(29.1 \frac{\text{J}}{\text{mol K}}\right) + (1)\left(28.8 \frac{\text{J}}{\text{mol K}}\right) - (1)\left(8.5 \frac{\text{J}}{\text{mol K}}\right) - (1)\left(33.6 \frac{\text{J}}{\text{mol K}}\right)$$

$$\Delta C_{P,\text{rxn}} = 15.8 \frac{\text{J}}{\text{mol K}}$$

$$\Delta H_{\text{reaction}}^\circ(T = 398.15\text{K}) = 131.28 + \int_{T=298.15\text{K}}^{T=398.15\text{K}} \Delta C_{P,\text{rxn}} dT = 131.28 + \left(0.0158 \frac{\text{kJ}}{\text{mol K}}\right)(100\text{K}) = 132.86 \frac{\text{kJ}}{\text{mol}}$$

NAME: \_\_\_\_\_

4. (20 Points) Calculate  $\Delta S_{\text{system}}$ ,  $\Delta S_{\text{total}}$ , and  $\Delta S_{\text{surroundings}}$  when the volume of 85.0 g of CO initially at 298K and 1 bar increases by a factor of 3 in three separate processes:

- Adiabatic, reversible expansion
- Isothermal expansion against external pressure,  $P_{\text{ext}}=0$
- Isothermal, reversible expansion

For each process, state if it is spontaneous or non-spontaneous.

Assume molar heat capacity of CO is constant and equal to  $C_{p,m} = 29.14 \text{ J mol}^{-1} \text{ K}^{-1}$ . Assume ideal gas behavior. The temperature of the surroundings is  $T=298\text{K}$ .

Solution:

a). adiabatic, reversible expansion

$q_{\text{system}}=0$  (adiabatic); thus  $\Delta S_{\text{system}}=0$  because the process is reversible.

$q_{\text{surroundings}}=0$  (adiabatic);  $\Delta S_{\text{surroundings}}=0$

$$\Delta S_{\text{total}}=0$$

not spontaneous

b). isothermal expansion against  $P_{\text{ext}}=0$ .

$\Delta U=0$  (isothermal process for ideal gas);  $w = 0$  (irreversible expansion against zero pressure); thus  $q_{\text{irreversible}}$  is zero. We need to find a reversible path to determine the entropy change of the system. The reversible compression at constant temperature is the path we choose. The reversible heat for this process is equal to the reversible work (the internal energy change is zero for ideal gas at constant temperature).

$$\Delta S_{\text{system}}^{\text{reverse process}} = \int \frac{\delta q_{\text{rev}}}{T} = \int_{V_f}^{V_i} nR d(\ln V) = nR \ln\left(\frac{V_i}{V_f}\right)$$

$$\Delta S_{\text{system}}^{\text{reverse process}} = \frac{85.0\text{g}}{28.01 \text{ g mol}^{-1}} \times 8.314 \frac{\text{J}}{\text{mol K}} \times \ln\left(\frac{1}{3}\right)$$

$$\Delta S_{\text{system}}^{\text{forward process}} = -\Delta S_{\text{system}}^{\text{reverse process}} = \frac{85.0\text{g}}{28.01 \text{ g mol}^{-1}} \times 8.314 \frac{\text{J}}{\text{mol K}} \times \ln(3)$$

$$= 27.7 \text{ J K}^{-1}$$

$$\Delta S_{\text{surroundings}}^{\text{forward process}} = 0 \text{ (system and surroundings exchange no heat during the irreversible expansion)}$$

$$\Delta S_{\text{total}} = 27.7 \text{ J K}^{-1} \text{ (spontaneous)}$$

NAME: \_\_\_\_\_

c). in this case, the system and surroundings exchange heat. since the forward process is reversible, we can use the relation between heat and work (since internal energy change is 0) to obtain the entropy change for the system.

$$\Delta S_{\text{system}}^{\text{forward process}} = \frac{q_{\text{rev}}}{T} = \frac{-w_{\text{rev}}}{T} = nR \ln \left( \frac{V_f}{V_i} \right)$$

$$\Delta S_{\text{system}}^{\text{forward process}} = \frac{85.0 \text{ g}}{28.01 \text{ g mol}^{-1}} \times 8.314 \frac{\text{J}}{\text{mol K}} \times \ln(3) = 27.7 \text{ J K}^{-1}$$

$$\Delta S_{\text{surroundings}}^{\text{forward process}} = \frac{-q_{\text{rev}}}{T} \text{ (system and surroundings exchange heat during the irreversible expansion)}$$

$$= -27.7 \text{ J K}^{-1}$$

$$\Delta S_{\text{total}} = 0 \quad \text{(not spontaneous)}$$

The system and surroundings are in equilibrium.

NAME: \_\_\_\_\_

5. (20 Points). The isothermal compressibility is defined as:

$$\kappa = -\frac{1}{V_m} \left( \frac{\partial V_m}{\partial P} \right)_T$$

where  $V_m$  is molar volume. Derive an expression for the isothermal compressibility in terms of pressure, temperature, and molar volume using the equation of state for a van der Waals gas.

$$\kappa = -\frac{1}{V_m} \left( \frac{\partial V_m}{\partial P} \right)_T =$$

$$\frac{1}{\kappa} = -V_m \left( \frac{\partial P}{\partial V_m} \right)_T$$

Thus, we need to find the appropriate derivative:

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$\left( \frac{\partial P}{\partial V_m} \right)_T = \frac{-RT}{(V_m - b)^2} + \frac{2a}{V_m^3}$$

$$\frac{1}{\kappa} = \frac{V_m RT}{(V_m - b)^2} - \frac{2a}{V_m^2}$$

$$\kappa = \left( \frac{V_m RT}{(V_m - b)^2} - \frac{2a}{V_m^2} \right)^{-1}$$

NAME: \_\_\_\_\_

**6. (10 Extra Credit Points)** In class, we discussed the entropy change for mixing of two different ideal gases, each initially confined to a separate compartment of a container. We saw that this entropy of mixing was positive, thus indicating a spontaneous process. Discuss the value of the entropy change associated with a mixing process in which the **same** gas is initially confined in two separate compartments, and then allowed to mix upon removal of the partition.

Solution:

Entropy change is 0 unlike the case for mixing of two different ideal gases.

The fact that the particles of the gas are indistinguishable leads to the zero entropy change, unlike in the case where two different gases mix. In the latter case, the particles are distinguishable (i.e., particles of A and particles of gas B), and thus the entropy change accounts for the “volume” doubling for each gas upon the mixing.