

Instructions: There are 5 questions for a total of 100 points. Please make sure to present your solutions in a clear, logical, and legible manner. Indicate your final answer(s) where appropriate. If you use scratch paper, remember to transfer answers to the exam; answers on scratch paper will not be considered. You are allowed use of pen/pencil, equations handbook, and calculator.

1A. (10 Points) For a fluid described by the following equation of state,

$$P = \frac{nRT}{V-b} - \frac{n^2a}{V^2}$$

the Joule-Thompson coefficient, μ_{J-T} , carefully formulated in the limit of low pressures (effectively, large molar volumes) as:

$$-\bar{C}_p \mu_{J-T} = b - \frac{2a}{RT}$$

where \bar{C}_p is the molar constant pressure heat capacity. For this scenario, what is the inversion temperature in terms of the parameters “a” and “b” as well as the gas constant, R.

Solution:

At the inversion temperature, the Joule-Thomson coefficient changes sign; thus, it equals zero. This allows us to determine the inversion temperature as:

$$-\bar{C}_p \mu_{J-T} = b - \frac{2a}{RT} = 0$$

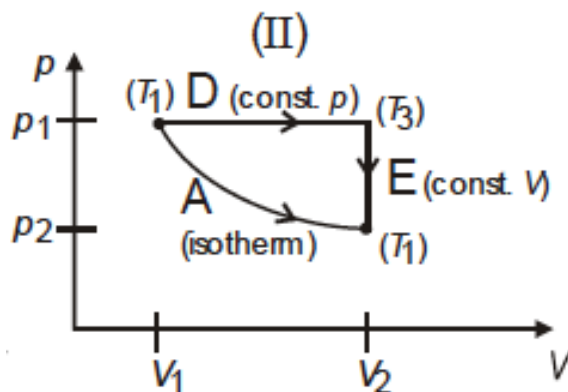
$$T_{inversion} = \frac{2a}{Rb}$$

1B. (5 Points) Consider a throttling process where the fluid undergoes adiabatic expansion with concomitant pressure decrease as the fluid passes through the constriction. If $\frac{2a}{RT} < b$, how does the temperature change during this process?

$$\mu_{J-T} = \frac{-1}{\bar{C}_p} \left(b - \frac{2a}{RT} \right) < 0$$

Thus, if pressure decreases, temperature increases.

2. (30 Points) Consider the following reversible processes (A, D, and E) for one mole of an ideal gas depicted on a P-V diagram:



Compute the following for each process (A, D, and E): q , w , ΔU , ΔH , $\int \frac{\delta q^{reversible}}{T}$.

[A] 1 mol gas (p_1, V_1, T_1) $\stackrel{const. T}{=} 1$ mol gas (p_2, V_2, T_1)

Ideal gas isotherm:

$$\Delta U_A = 0$$

$$\Delta H_A = 0$$

$$w_A = -RT_1 \ln \frac{V_2}{V_1} \quad q_A = RT_1 \ln \frac{V_2}{V_1} \quad \int \frac{\delta q}{T} = R \ln \frac{V_2}{V_1}$$

[D]

$$\Delta U_D = C_V(T_3 - T_1)$$

$$\Delta H_D = C_P(T_3 - T_1)$$

$$q_D = C_P(T_3 - T_1)$$

$$w_D = -R(T_3 - T_1)$$

$$\int \frac{\delta q_D}{T} = C_P \ln \left(\frac{T_3}{T_1} \right)$$

[E]

$$\Delta U_E = C_V(T_1 - T_3)$$

$$\Delta H_E = C_P(T_1 - T_3)$$

$$w_E = 0$$

$$q_E = C_V(T_1 - T_3)$$

$$\int \frac{\delta q_E}{T} = C_V \ln \left(\frac{T_1}{T_3} \right)$$

[A] vs. [D] + [E]

$$\Delta U_A = 0$$

$$\Delta U_D + \Delta U_E = \Delta U_A$$

$$\Delta H_A = 0$$

$$\Delta H_D + \Delta H_E = \Delta H_A$$

$$q_A = RT_1 \ln \frac{V_2}{V_1}$$

$$q_D + q_E = R(T_3 - T_1) \neq q_A$$

$$w_A = -RT_1 \ln \frac{V_2}{V_1}$$

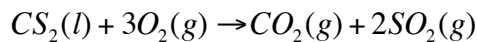
$$w_D + w_E = -R(T_3 - T_1) \neq w_A$$

$$\int \frac{\delta q_A}{T} = R \ln \frac{V_2}{V_1}$$

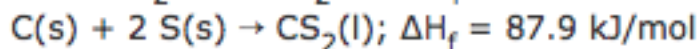
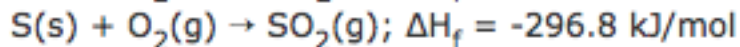
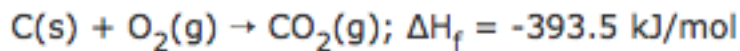
$$\int \frac{\delta q_D}{T} + \int \frac{\delta q_E}{T} = R \ln \left(\frac{V_2}{V_1} \right) = \int \frac{\delta q_A}{T}$$

Here again $\left(\int \frac{\delta q_{rev}}{T} \right)$ looks like a state function!

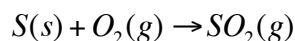
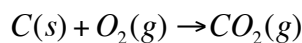
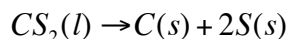
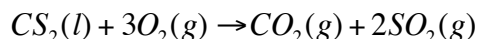
3A. (10 Points) For the following reaction:



determine the constant pressure heat of reaction. The following data may be helpful.



Solution: Using the property that enthalpy is a state function, the following ordering of the given reactions allows us to recover the reaction of interest:



The enthalpy of reaction is obtained by adding the reaction enthalpies of the reactions as written in the given ordering of reactions:

$$\begin{aligned} \Delta H &= (\Delta H_{f,rxn1} + 2\Delta H_{f,rxn2} - \Delta H_{f,rxn3}) \\ &= (-393.5 - (2)(296.8) - 87.9) \frac{\text{kJ}}{\text{mol}} \\ &= -1075.0 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

3B. (10 Points) At 298K, the enthalpy of denaturation of hen egg white lysozyme is +217.6 kJ/mol and the change in constant-pressure molar heat capacity resulting from the denaturation of the protein is +6.3 kJ/mol. Provide an estimate of the denaturation enthalpy for reversible denaturation of hen egg-white lysozyme at 351K. Discuss any assumptions you make in order to provide an estimate.

Solution:

For this question, we can use the relation for the variation of enthalpy of reaction with temperature on page 5-10 of the Equations Handbook. Assuming that the change in constant pressure molar heat capacity does not vary with temperature over the range involved, we can write:

$$\begin{aligned} \Delta H_{reaction}(T = 351K) &= \Delta H_{reaction}(T = 298K) + \int_{298K}^{351K} \Delta C_{P,denaturation} dT \\ &= \Delta H_{reaction}(T = 298K) + \Delta C_{P,denaturation} \int_{298K}^{351K} dT = \Delta C_{P,denaturation} (351 - 298) \\ &= 6.3 \frac{\text{kJ}}{\text{mol} - K} (351K - 298K) = 551.5 \text{ kJ/mol} \end{aligned}$$

4A. **(5 Points)** An ideal gas at equilibrium is contained in a piston assembly initially at a state point described by P_1 , T_1 , and V_1 . The piston head is held in place by stoppers as the external pressure equals zero. The stoppers are removed and the ideal gas expands until the piston head encounters another set of stoppers at a new volume V_2 . The gas then equilibrates to T_2 and P_2 . The process is adiabatic. What is the change in internal energy? State any assumptions you must make in order to solve the problem.

Solution:

For an ideal gas, the internal energy depends only on temperature. Assuming that the constant volume heat capacity is temperature independent (or at least varies slightly over the temperature range of interest), we can write the change in internal energy as:

$$dU = C_v dT$$

$$\Delta U = C_v (T_2 - T_1)$$

4B. **(15 Points)** Two moles of Ne gas, initially at 30Celsius, is compressed from an initial volume of 20.0L to a final volume of 15 L. Calculate the change in internal energy, heat interaction, work interaction, and final temperature, T_2 for this compression done adiabatically with constant external pressure of 1 atm.

Solution:

The heat interaction is zero since this is an adiabatic process.

The work interaction is given by the mechanical expression for work:

$$\delta w = -p_{\text{external}} dV$$

$$w = -p_{\text{external}} (V_2 - V_1) = -(1\text{atmosphere})(15L - 20L)$$

$$= 5 L \cdot \text{atm} = 5 L \cdot \text{atm}(101.325J/L \cdot \text{atm})$$

$$= 506.6J$$

For the change in internal energy, we consult the First Law:

$$dU = \delta q + \delta w = 0 + \delta w$$

Recall from class discussion that in this case, we are equating a state function to a path-dependent function. This requires care. To determine the actual change in internal energy, we need to effect the change from V_1 to V_2 in a reversible way. For an adiabatic, reversible compression, we have from previous class lectures:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

$$T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1} = 303K \left(\frac{20L}{15L} \right)^{(5/3)-1} = 367K$$

For Ideal gas, the internal energy is dependent on the final temperature:

$$\Delta U = C_v (T_2 - T_1) = \frac{3}{2} R (367 - 303) = 1596.3J$$

Thus, since the compression is adiabatic, the system gains energy (consistent with the higher final temperature)

5. (15 Points) Fill in the blank; true or false.

A. Joule's Free expansion is an experiment with a **constant internal energy** constraint.

B. An **ideal gas thermometer** allows us to define an absolute temperature scale with one reference point being the **triple point of water**.

C. The internal energy change for an adiabatic process in which no work interaction is involved is path dependent. FALSE?

D. A thermodynamic state function that allows us to account for pressure-volume work is _____ **Enthalpy** _____.

E. Considering total system volume to be a state function of temperature and pressure, the total differential of volume, "dV", can be written in the most general form as:

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$