

Directions: Please answer each question to the best of your ability. Make sure your response is **legible, precise, includes relevant dimensional units (where appropriate), logically presented (include non-mathematical language if necessary to convey your intent clearly and transparently), and correct/accurate**. You are free to use your Equations Handbook, Calculator, blunt/sharp writing instrument, and brain (your choice). If you have any doubt(s) about the meaning/intent of a question(s), please ask immediately so you do not wander off on an incorrect path! **Please leave all responses to be graded on the exam sheet. Work on scratch paper will not be considered.**

Problem	Points
1	/10
2	/15
3	/30
4	/10
5	/15
6	/20
Total	/100

1 (10 Points) Matching / Fill-In. Provide the proper response from the right column in the blanks provided in the left column. *Keep in mind that some blanks in the left column may require multiple selections from the choices in the right column.*

1. Joule-Thomson expansion for cooling is a reversible process. True or False? _____ H	A internal energy
2. Functional mathematical relationships between state variables such as pressure, volume, temperature are called _____ K .	B entropy
3. The Joule Coefficient for an Ideal Gas is _____ P	C state function
4. Molar properties are _____ L , being independent of system size.	D isenthalpic
5. The first law relates changes in a system's internal energy to changes in a system's heat and work, Δq and Δw , respectively. True or False? _____ H	E isothermal expansion
6. The _____ J 'Law' provides an explanation of the asymmetry of 'natural' processes.	F adiabatic expansion
7. Total entropy change for an irreversible adiabatic process must be zero. True or False? _____ H	G true
8. The stages of a Carnot Cycle are _____ E, F, I, M	H false
9. The Joule-Thomson Expansion process is an _____ D process.	I adiabatic compression
10. Ideal gas _____ A, N is(are) function(s) of temperature only.	J second
	K equations of state
	L intensive
	M isothermal compression
	N enthalpy
	O isentropic cooling
	P zero
	Q extensive
	R first order

2. (15 Points) For a fluid described by the ideal gas equation of state, show that the following relation holds: $\left(\frac{\partial U}{\partial P}\right)_T = 0$. Begin with the following relation for the total differential of $U(T,V(T,P))$, $dU(T,V(T,P)) = C_v(T) dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV$ where P is pressure, T is temperature, V is volume, $C_v(T)$ is the constant volume heat capacity, and U is internal energy.

Solution:

In the general case, where $U=U(T,V(T,P))$, we can write:

$$\begin{aligned}\left(\frac{\partial U}{\partial P}\right)_T &= \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_T + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T \\ &= C_v(T) \left(\frac{\partial T}{\partial P}\right)_T + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T\end{aligned}$$

The first partial is zero since it is taken at constant temperature. In order to obtain $\left(\frac{\partial U}{\partial V}\right)_T$, we can use the given relation for the **total differential of U, dU**, under constant temperature conditions:

$$\begin{aligned}dU(T,V(T,P)) &= 0 + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV \\ \left(\frac{\partial U}{\partial V}\right)_T &= \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]\end{aligned}$$

Thus, we have:

$$\begin{aligned}\left(\frac{\partial U}{\partial P}\right)_T &= 0 + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]\left(\frac{\partial V}{\partial P}\right)_T \\ &= \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]\left(\frac{\partial V}{\partial P}\right)_T\end{aligned}$$

Use the ideal gas EOS to evaluate the partial derivatives needed:

$$\begin{aligned}\left(\frac{\partial U}{\partial P}\right)_T &= \left[\left(\frac{nRT}{V}\right) - \left(\frac{nRT}{V}\right)\right]\left(\frac{\partial V}{\partial P}\right)_T \\ &= 0\end{aligned}$$

3A. (25 Points) It can be shown that the Joule-Thomson coefficient can be expressed as:

$$\mu_{JT} = \frac{1}{C_{P,molar}} \left[T \left(\frac{\partial \bar{V}}{\partial T} \right)_P - \bar{V} \right]$$

Where P is pressure, T temperature, and \bar{V} molar volume. The constant pressure specific heat is given as a molar property in this equation. For a fluid described by the Van der Waals equation of state, derive an equation for the inversion temperature. In the final stages of your analysis, you will need to consider the above equation under limiting conditions of $\bar{V} \rightarrow \infty$.

Solution:

We are given an expression for the Joule-Thomson coefficient, which should be a function of temperature at a particular pressure. We need to find the temperature where this value is zero, the inversion temperature. We must first evaluate the expression using the Van der Waals EOS. We first apply the cyclic 'rule' to obtain an expression in terms of partial derivatives that are easier to work with as follows:

$$\begin{aligned} \mu_{JT} &= \frac{1}{C_{P,molar}} \left[T \left(\frac{\partial \bar{V}}{\partial T} \right)_P - \bar{V} \right] \\ &= \frac{1}{C_{P,molar}} \left[-T \left(\frac{\partial P}{\partial T} \right)_V - \bar{V} \right] \\ &= \frac{1}{C_{P,molar}} \left[-T \left(\frac{\partial P}{\partial V} \right)_T - \bar{V} \right] \end{aligned}$$

Evaluate the partial derivatives for the VdW EOS:

VdW :

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

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{R}{\bar{V} - b} \quad \rightarrow \quad -T \left(\frac{\partial P}{\partial T} \right)_V = \frac{-RT}{\bar{V} - b}$$

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

$$\begin{aligned} \mu_{JT} &= \frac{1}{C_{P,molar}} \left[\frac{-RT}{\bar{V} - b} - \bar{V} \right] = \frac{1}{C_{P,molar}} \left[\frac{-RT}{(\bar{V} - b)^2 + \frac{2a}{\bar{V}^3}} - \bar{V} \right] \\ &= \frac{1}{C_{P,molar}} \left[\frac{-RT(\bar{V} - b)\bar{V}^3}{-RT\bar{V}^3 + 2a(\bar{V} - b)^2} - \bar{V} \right] = \frac{1}{C_{P,molar}} \left[\frac{-RT(\bar{V} - b)\bar{V}^3}{-RT\bar{V}^3 + 2a(\bar{V} - b)^2} - \bar{V}(1) \right] \\ &= \frac{1}{C_{P,molar}} \left[\frac{-RT(\bar{V} - b)\bar{V}^3}{-RT\bar{V}^3 + 2a(\bar{V} - b)^2} - \bar{V} \left(\frac{-RT\bar{V}^3 + 2a(\bar{V} - b)^2}{-RT\bar{V}^3 + 2a(\bar{V} - b)^2} \right) \right] = \frac{1}{C_{P,molar}} \left[\frac{-RT(\bar{V} - b)\bar{V}^3 - \bar{V}(-RT\bar{V}^3 + 2a(\bar{V} - b)^2)}{-RT\bar{V}^3 + 2a(\bar{V} - b)^2} \right] \\ &= \frac{1}{C_{P,molar}} \left[\frac{-RT\bar{V}^4 + RTb\bar{V}^3 + RT\bar{V}^4 - 2a\bar{V}^3 + 4ab\bar{V}^2 - 2ab^2\bar{V}}{-RT\bar{V}^3 + 2a(\bar{V} - b)^2} \right] \\ &= \frac{1}{C_{P,molar}} \left[\frac{RTb\bar{V}^3 - 2a\bar{V}^3 + 4ab\bar{V}^2 - 2ab^2\bar{V}}{-RT\bar{V}^3 + 2a(\bar{V} - b)^2} \right] \end{aligned}$$

Now, we consider that in the limit of molar volume going to infinity (as stated in the problem), the terms that remain are the cubic terms; we thus are left with:

$$= \frac{1}{C_{P,molar}} \left[\frac{RTb\bar{V}^3 - 2a\bar{V}^3}{-RT\bar{V}^3} \right] = \frac{1}{C_{P,molar}} \left[\frac{RTb - 2a}{-RT} \right] = \mu_{JT}$$

Setting equal to zero gives:

$$0 = \frac{1}{C_{P,molar}} \left[\frac{RTb - 2a}{-RT} \right]$$

$$\frac{RTb - 2a}{-RT} = 0$$

$$RTb - 2a = 0$$

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

3B (5 Points). Using the relation for the Joule-Thomson Coefficient, $\mu_{JT} = \frac{1}{C_{P,molar}} \left[T \left(\frac{\partial \bar{V}}{\partial T} \right)_P - \bar{V} \right]$, determine

the numerical value for $\mu_{JT}^{\text{Ideal Gas}}$. Present your work in a logical, systematic manner, and show all steps explicitly.

IG:

$$\bar{V} = \frac{RT}{P}$$

$$\left(\frac{\partial \bar{V}}{\partial T} \right)_P = \frac{R}{P} \rightarrow T \left(\frac{\partial \bar{V}}{\partial T} \right)_P = \frac{RT}{P}$$

$$\mu_{JT} = \frac{1}{C_{P,molar}} \left[T \left(\frac{\partial \bar{V}}{\partial T} \right)_P - \bar{V} \right] = \frac{1}{C_{P,molar}} \left[\frac{RT}{P} - \frac{RT}{P} \right] = 0$$

4 (10 Points) An ideal gas is originally confined in a volume V_1 within an insulated container whose total volume is (V_1+V_2) . The remaining container volume is evacuated. The partition separating the volumes is removed allowing the gas to expand to fill the entire container. If the initial temperature of the gas is T , what is the final temperature? Use equations to justify your answer.

Solution:

Since the container is insulated, we consider an adiabatic process. We consider as our system the gas. Thus, since the expansion occurs against vacuum, we have:

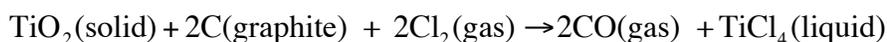
$$dU = dq + dw = 0 - p_{ext}dV = 0$$

However, for an ideal gas:

$$dU = C_v dT$$

Thus, since $dU=0$ and $C_v>0$, we have $dT=0$. Integrating for the process, we have $\Delta T=0$. Thus the final temperature is T as well.

5A (7.5 Points) The standard reaction enthalpy for the following reaction,



at 298K is -80.0 kJ/mol. Use the following data to estimate the standard enthalpy at 135.8 Celsius.

	TiO ₂ (solid)	Cl ₂ (gas)	C(graphite)	CO(gas)	TiCl ₄ (liquid)
$\Delta_f H^\circ$ (kJ/mol)	-945			-110.5	
$C_{P,m}$ (J mol ⁻¹ K ⁻¹)	55.06	33.91	8.53	29.12	145.2

$$\begin{aligned} \Delta H^\circ(135.8^\circ\text{C}) &= \Delta H^\circ(25^\circ\text{C}) + \int_{298\text{K}}^{408.95} \Delta C_{P,molar} dT \\ &= \Delta H^\circ(25^\circ\text{C}) + \Delta C_{P,molar} \int_{298\text{K}}^{408.95} dT = \Delta H^\circ(25^\circ\text{C}) + \Delta C_{P,molar} \Delta T \end{aligned}$$

where we assume the change in specific heats is independent of temperature. Substituting values, we obtain:

$$\begin{aligned} \Delta H^\circ(138.5^\circ\text{C}) &= \Delta H^\circ(25^\circ\text{C}) + \Delta C_{P,molar} \Delta T \\ &= -80.0 \frac{\text{kJ}}{\text{mol}} + \left((1)(145.2 \frac{\text{J}}{\text{mol K}} + (2)(29.12 \frac{\text{J}}{\text{mol K}} - (1)(55.06 \frac{\text{J}}{\text{mol K}}) - (2)(8.53 \frac{\text{J}}{\text{mol K}}) - (2)(33.91 \frac{\text{J}}{\text{mol K}}) \right) \Delta T \\ &= -80.0 \frac{\text{kJ}}{\text{mol}} + (0.0635 \frac{\text{kJ}}{\text{mol K}})(408.95\text{K} - 298\text{K}) \\ &= -80.0 \frac{\text{kJ}}{\text{mol}} + 7.05 \frac{\text{kJ}}{\text{mol}} \\ &= -72.95 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

5B (7.5 Points) In an experiment to estimate 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. Give an estimate of 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.

Considering that the system including calorimeter and foodstuffs is isolated, $dU_{\text{Total}}=0$. Thus, the heat liberated from oxidation is used to heat the calorimeter, thus causing temperature increase of the calorimeter. We need the heat capacity (calorimeter constant from Engel & Reid terminology), which is determined from the information about how much temperature rise occurs upon application of a certain amount of current. First, to determine the calorimeter constant:

$$\begin{aligned} C_{cal} &= \frac{q}{\Delta T} = \frac{IVt}{\Delta T} = \frac{(1.27\text{A})(12.5\text{V})(157\text{s})}{3.88^\circ\text{C}} = \frac{2492.4\text{AVs}}{3.88^\circ\text{C}} = \frac{2492.4 \frac{\text{J}}{\text{s}}}{3.88^\circ\text{C}} = \frac{2492.4\text{J}}{3.88^\circ\text{C}} \\ &= 642.4 \frac{\text{J}}{^\circ\text{C}} \end{aligned}$$

Thus, oxidation of the foodstuffs giving rise to 2.80 Celsius rise in calorimeter temperature leads to

$$q = C_{cal} \Delta T = (642.4 \frac{\text{J}}{^\circ\text{C}})(2.89^\circ\text{C}) = 1856.4\text{J}$$

6 (20 Points) For the following questions, state any assumption(s) you make. Take the specific heat at constant volume as $C_V = 5 \frac{\text{cal}}{\text{mol } ^\circ\text{C}}$ and $R = 2 \frac{\text{cal}}{\text{mol } ^\circ\text{C}}$

A. How much heat is required to raise the temperature of 1000 grams of nitrogen from -20C to 100C at constant pressure?

Considering nitrogen to follow ideal gas behavior over this temperature range, the heat required is:

$$q_P = n(C_V + R)\Delta T = \left(\frac{1000\text{gr}}{28\text{gr/mole}}\right)\left(5 \frac{\text{cal}}{\text{mole } ^\circ\text{C}} + 2 \frac{\text{cal}}{\text{mole } ^\circ\text{C}}\right)(120^\circ\text{C}) = 30000\text{cal} = 30\text{kcal}$$

B. What is the change in internal energy?

$$\Delta U = n(C_V)\Delta T = \left(\frac{1000\text{gr}}{28\text{gr/mole}}\right)\left(5 \frac{\text{cal}}{\text{mole } ^\circ\text{C}}\right)(120^\circ\text{C}) = 21429\text{cal} = 21.429\text{kcal}$$

C. How much external work was done?

$$w = q - \Delta U = n(C_V)\Delta T = 30\text{kcal} - 21.429\text{kcal} = 8.6\text{kcal}$$

D. How much heat is required if volume is kept constant?

$$q_V = n(C_V)\Delta T = \left(\frac{1000\text{gr}}{28\text{gr/mole}}\right)\left(5 \frac{\text{cal}}{\text{mole } ^\circ\text{C}}\right)(120^\circ\text{C}) = 21429\text{cal} = 21.429\text{kcal}$$