

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) As precisely as possible, calculate the molar volume of CO₂ when it is subject to a pressure of 10 bar at 100°C. Consider the gas to obey the van der Waals equation of state.

As precisely as possible, calculate the molar volume of CO₂ under the same conditions by the van der Waals gas law.

As the equation of van der Waals is a third-order equation in molar volume, one must solve for the answer either by iteration or by using a complex computation. One way to approach the solution is to use the iteration method:

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

One iterates this equation until the volumes are the same, using some initial guess for the volume. I choose to start with the volume that comes out of the ideal-gas calculation:

$$\begin{aligned} V_m^{(2)} &= \frac{8.3144349 \text{ JK}^{-1} \text{ mol}^{-1} (373.15 \text{ K})}{1 \times 10^6 \text{ Pa} + \frac{0.3658 \text{ Pa m}^6 \text{ mol}^{-2}}{(3.1025 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1})^2}} + 42.8588 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1} \\ &= 3.0318 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1} \end{aligned}$$

This is fairly close to the initial guess, but let's iterate again.

$$\begin{aligned} V_m^{(2)} &= \frac{8.3144349 \text{ JK}^{-1} \text{ mol}^{-1} (373.15 \text{ K})}{1 \times 10^6 \text{ Pa} + \frac{0.3658 \text{ Pa m}^6 \text{ mol}^{-2}}{(3.0318 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1})^2}} + 42.8588 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1} \\ &= 3.0266 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1} \end{aligned}$$

That is still not exactly consistent. A third iteration gives $3.0263 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$. A fourth iteration gives $3.0263 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$. The operation has now converged to a consistent answer.

**DO NOT WRITE
IN THIS SPACE**

1 _____/20

2,3 _____/30

4,5 _____/20

6,7 _____/30

8 _____/5
(Extra credit)

TOTAL PTS

/100

2. (20 points) Enter a word or phrase that is best described by the definition to the right.

	Answer	Definition
A.	SYSTEM	Part of the universe in which the experimenter is interested.
B.	STATE	The condition of a system, as enumerated by properties.
C.	OPEN SYSTEM	A system that can exchange matter <u>and</u> energy with its surroundings.
D.	ZEROTH LAW	Two systems in thermal equilibrium with a third system are also in thermal equilibrium with each other.
E.	INTENSIVE PROPERTIES	Properties that do not depend on the amount of material present.
F.	CORRESPONDING STATES	Different gases have the same equation of state if each gas is described by the dimensionless reduced variables.
G.	FIRST LAW	The internal energy of an isolated system is constant.
H.	THERMODYNAMICS	The branch of science that describes the behavior of matter and the transformation between different forms of energy on the macroscopic scale.
I.	PRESSURE	Force per unit area.
J.	HEAT	The quantity of energy that flows across the boundary between the system and surroundings because of a temperature difference between the system and surroundings.

3. (10 points) The quality of approximate gas laws is assessed by how well they reproduce experimental measurements. The following equation for a gas's critical temperature is given in terms of the van der Waals parameters of the gas:

$$T_c = \frac{8a}{27bR}$$

Using this equation, calculate the critical temperature of CHCl_2F from its van der Waals parameters. How well does this agree with the reported experimental value? [Note: CHCl_2F , known as HCFC-21, is used as a refrigerant; knowing its gas-phase properties is of some practical importance.]

The critical temperature is calculated by direct substitution:

$$T_c = \frac{8a}{27bR} = \frac{8(1.1481 \text{ Pa m}^6 \text{ mol}^{-2})}{27(90.6041 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1})(8.3144349 \text{ JK}^{-1} \text{ mol}^{-1})}$$

$$= 451.58 \text{ K}$$

The reported value from the handbook is exactly that! (Hmmm, I'll bet that the data in the book was calculated from the van der Waals equation, and perhaps not really measured.)

4. (10 points) For each expression given in the left column, choose the appropriate description from the right column and indicate its letter in blank to the left of the expression.

a $q = 0$	a) Adiabatic process b) Average speed c) Boltzmann factor d) Chain rule e) Cyclic rule f) First law of thermodynamics g) Galileo's law of gravitation h) Heat capacity for an ideal gas i) Heat capacity for any liquid j) Heat capacity for any solid k) Indicator diagram l) Joule's law of electrical heating m) Joule-Thomson coefficient n) Law of Dulong and Petit o) Most probable speed p) Shomate equation q) Sutherland potential r) Zero th law of thermodynamics
e $\left(\frac{\partial U}{\partial T}\right)_P = -\left(\frac{\partial U}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_U$	
l $q = I^2 R t$	
c $p_i = \frac{e^{-\epsilon_i / kT}}{\sum_j e^{-\epsilon_j / kT}}$	
b $\int_0^{\infty} v f(v) dv$	

5. (10 points) Determine the amount of heat required to raise the temperature of 1.768 moles of liquid Ni from 2000 K to 2500 K, as accurately as you can. [Assume that the pressure remains constant at 1 bar during the process.]

We use the heat capacity of nickel, which is given in Table 5.6. of your Handbook. $C_{Pm}^{\theta} = 38.91103 \text{ J K}^{-1} \text{ mol}^{-1}$. For one mole, the heat required is

$$q_m = \int_{2000 \text{ K}}^{2500 \text{ K}} C_{Pm}^{\theta} dT = \int_{2000 \text{ K}}^{2500 \text{ K}} 38.91103 \text{ J K}^{-1} \text{ mol}^{-1} dT = 38.91103 \text{ J K}^{-1} \text{ mol}^{-1} (2500 \text{ K} - 2000 \text{ K}) = 19,455.515 \text{ J mol}^{-1}$$

But the question asks for the amount of heat required to heat 1.768 moles.

$$q = n q_m = 1.768 \text{ mol} (19,455.515 \text{ J mol}^{-1}) = 34.40 \text{ kJ}$$

6. (10 points) Consider throwing a pair of dice. (a) What is the probability that, on one throw, the sum of the two dice is 7?

Each combination has a chance of 1/36. There are several combinations that lead to 7: 6,1; 5,2; 4,3; 3,4; 2,5, 1,6. Thus, the probability of obtaining 7 on one throw is

$$P(7) = 6 \left(\frac{1}{36} \right) = \frac{1}{6}$$

(b) What is the probability that, on two sequential tosses of the two dice (as one might do in a game of craps), the sum of the two dice is 7 on both the first and the second throw?

Each throw has the same probability (1/6), so the probability of two in a row is just:

$$P(7;7) = P(7)P(7) = \left(\frac{1}{6} \right) \left(\frac{1}{6} \right) = \frac{1}{36}$$

7. (10 points) One mole of a monatomic ideal gas is carried through the following sequence of reversible steps: (a) heated at constant volume from 298.15 K and 1 bar to 373.15K; (b) expanded to twice its original molar volume while holding the temperature constant; (c) cooled from 373.15 K and the new volume reversibly back to 298.15 K and 1 bar. Give results for the following:

(1) Heat transfer in step (a)	$\frac{3}{2}R\Delta T = \frac{3}{2}(8.3144349 \text{ J K}^{-1})(75 \text{ K}) = 935.37393 \text{ J}$
(2) Change in the energy in step (a)	$\frac{3}{2}R\Delta T = \frac{3}{2}(8.3144349 \text{ J K}^{-1})(75 \text{ K}) = 935.37393 \text{ J}$
(3) Work done in step (a)	0 J
(4) Total heat transferred in the whole process	$q = q_a + q_b + q_c = 935.37393 \text{ J} + q_c = -w_c$
(5) Total work done on the gas in the whole process	$w = w_a + w_b + w_c = -2,150.511 \text{ J} + w_c$

In step (a) there is no work, so $q_a = \Delta U_a = 935.37393 \text{ J}$

In step (b) $\Delta U_b = 0$, so $q_b = -w_b = RT \ln \left(\frac{V_f}{V_i} \right) = (8.3144349 \text{ J K}^{-1} \text{ mol}^{-1})(373.15 \text{ K}) \ln(2) = 2,150.511 \text{ J}$

In step (c), both T and V are changing reversibly, but one does not have a specification of the path (by telling exactly how one or the other changes). Since it brings the back to the original state, $\Delta U_c = -935.37393 \text{ J} - 0 \text{ J} = -935.37393 \text{ J}$. Since q_c and w_c depend on the path (which is not exactly known), the best one can do is express the effect in terms of one or the other. In the table, I have expressed it in terms of the work done in step (c). One could also express it in terms of the heat transfer in step (c), which would also be correct.

8. (5 points, extra credit) Starting with the definition of the appropriate state functions, show that the heat capacity at constant pressure can be expressed in the following manner:

$$C_{Pm} = \left(\frac{\partial U_m}{\partial T} \right)_p + P \left(\frac{\partial V_m}{\partial T} \right)_p$$

Start with the definition of the enthalpy:

$$H_m = U_m + PV_m$$

Take the partial derivative of this with respect to temperature at constant pressure:

$$\left(\frac{\partial H_m}{\partial T} \right)_p = \left(\frac{\partial U_m}{\partial T} \right)_p + \left(\frac{\partial PV_m}{\partial T} \right)_p = \left(\frac{\partial U_m}{\partial T} \right)_p + P \left(\frac{\partial V_m}{\partial T} \right)_p + V_m \left(\frac{\partial P}{\partial T} \right)_p$$

Then one identifies the derivative on the left as the molar heat capacity at constant pressure:

$$C_{Pm} = \left(\frac{\partial U_m}{\partial T} \right)_p + P \left(\frac{\partial V_m}{\partial T} \right)_p + V_m \left(\frac{\partial P}{\partial T} \right)_p$$

The last derivative is zero because it is the derivative of something held constant. Hence, one gets to the form requested:

$$C_{Pm} = \left(\frac{\partial U_m}{\partial T} \right)_p + P \left(\frac{\partial V_m}{\partial T} \right)_p$$