

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. (15 points) Compare the pressure exerted by 1 mole of Ar enclosed in a 25 L cylinder at exactly 500 K with that exerted by 1 mole of ammonia at the same conditions predicted using van der Waals equation of state. How do these values compare with the ideal gas prediction and what can be said about these two gases being close to ideal at these conditions?

$$P(\text{Ar}) = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$= \frac{8.3144439 \frac{\text{J}}{\text{mol} \times \text{K}} \times 500\text{K}}{25 \frac{\text{L}}{\text{mol}} \times 10^{-3} \frac{\text{m}^3}{\text{L}} - 32.0130 \times 10^{-6} \frac{\text{m}^3}{\text{mol}}} - \frac{0.1355 \frac{\text{Pa} \times \text{m}^6}{\text{mol}^2}}{\left(25 \frac{\text{L}}{\text{mol}} \times 10^{-3} \frac{\text{m}^3}{\text{L}}\right)^2}$$

$$P(\text{Ar}) = 166501.9 \frac{\text{J}}{\text{m}^3} - 216.8 \text{Pa} = 166285.1 \text{Pa} = 1.641 \text{ atm}$$

$$P(\text{Ar})_{\text{ideal}} = \frac{RT}{V_m} = \frac{8.3144349 \frac{\text{J}}{\text{mol} \times \text{K}} \times 500\text{K}}{0.025 \frac{\text{mol}}{\text{m}^3}} = 166288.7 \text{Pa} = 1.641 \text{ atm}$$

$$P(\text{ammonia}) = \frac{8.3144349 \frac{\text{J}}{\text{mol} \times \text{K}} \times 500\text{K}}{25 \frac{\text{L}}{\text{mol}} \times 10^{-3} \frac{\text{m}^3}{\text{L}} - 37.1311 \times 10^{-6} \frac{\text{m}^3}{\text{mol}}} - \frac{0.4225 \frac{\text{Pa} \times \text{m}^6}{\text{mol}^2}}{\left(25 \frac{\text{L}}{\text{mol}} \times 10^{-3} \frac{\text{m}^3}{\text{L}}\right)^2} = 166536.0 \text{Pa} - 676.0 \text{Pa} =$$

$$= 165860.0 \text{Pa} = 1.637 \times \text{atm}$$

$$P(\text{ammonia})_{\text{ideal}} = \frac{RT}{V_m} = \frac{8.3144349 \frac{\text{J}}{\text{mol} \times \text{K}} \times 500\text{K}}{0.025 \frac{\text{mol}}{\text{m}^3}} = 166288.7 \text{Pa} = 1.641 \text{ atm}$$

At such a high temperature, the description of both gases using ideal gas law is very appropriate. Obviously, argon's behavior is closer to the ideal than ammonia's.

DO NOT WRITE IN THIS SPACE
p. 1 _____/15
p. 2 _____/10
p. 3 _____/10
p. 4 _____/15
p. 5 _____/10
p. 6 _____/10
p. 7 _____/15
p. 8 _____/15
=====
p. 9 _____/5 (Extra credit)
=====
TOTAL PTS

/100

2. (10 points) Match the best ending of the phrase from the right column with the beginning of the phrase from the left column:

1) Extensive properties __a__	a) Depend on the amount of a substance
2) The fact that the critical compressibility factor is nearly the same for all gases is stated by __d__	b) The molecules are hard spheres
3) One of the ideal gas law approximations is __l__	c) A gas cannot be compressed into a liquid at any pressure
4) The constant a in the van der Waals equation __h__	d) The law of corresponding states
5) Above the critical temperature __c__	e) Takes into account repulsive interactions
	f) Pigs fly
	g) A liquid cannot be evaporated at any pressure
	h) Takes into account attractive interactions
	i) Does not exist
	j) Collisions with a solid wall are inelastic
	k) The Maxwell-Boltzman distribution
	l) The molecules are point masses
	m) Are independent of the size of a system

3. (10 points) Calculate the change in entropy of 2 moles of xenon upon isothermal expansion at 298.15 K from 20 L until the pressure becomes exactly 1 bar. [HINT: Consider xenon to be an ideal gas.]

First, calculate the volume of the gas at the final point using the ideal-gas law.

$$V = \frac{nRT}{P} = \frac{2 \text{ mol} \times 8.3144349 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}{100000 \text{ Pa}} = 0.049579 \text{ m}^3 = 49.579 \text{ L}$$

In an isothermal expansion, the change in the entropy is given by

$$\int_{S_1}^{S_2} dS = nR \int_{V_1}^{V_2} \frac{1}{V} dV$$

Integration gives the following formula for the entropy change:

$$S_2 - S_1 = nR \ln\left(\frac{V_2}{V_1}\right).$$

Having calculated the final volume, one can easily obtain the numerical result:

$$S_2 - S_1 = 2 \text{ mol} (8.3144349 \text{ J K}^{-1} \text{ mol}^{-1}) \ln\left(\frac{49.579 \text{ L}}{20 \text{ L}}\right) = 15.096 \text{ J K}^{-1}$$

4. (15 point s) Consider oxygen in a cylinder at two atmospheres at a room temperature of 298.15 K. This oxygen is to be attached to a burner that requires an oxygen flow of ten grams per minute to keep a flame burning. What is the area of the pinhole that will allow this flow of oxygen? [You may assume that, at this pressure, oxygen can be treated as an ideal gas.]

This is a two-step problem. First calculate the number of moles of gas that must escape through the pinhole per minute

$$n = \frac{10 \text{ g/min}}{31.9988 \text{ g/mol}} = 0.312512 \frac{\text{mol}}{\text{min}}$$

This corresponds to exactly

$$N = 0.312512 \frac{\text{mol}}{\text{min}} (6.02211415 \times 10^{23} \frac{\text{molecules}}{\text{mol}}) (\frac{1 \text{ min}}{60 \text{ s}}) = 3.13664 \times 10^{21} \frac{\text{molecules}}{\text{s}}$$

This is the number of collisions with the hole that must be experienced per second to allow that many molecules to escape.

Second, calculate the wall collision frequency

$$\begin{aligned} Z_{\text{wall}} &= n^* \left(\frac{RT}{2\pi M} \right)^{1/2} = \frac{PL}{RT} \left(\frac{RT}{2\pi M} \right)^{1/2} \\ &= \frac{PL}{\sqrt{2RT\pi M}} = \frac{2 \text{ atm} \times 101325 \frac{\text{Pa}}{\text{atm}} \times 6.02211415 \times 10^{23} \frac{\text{molecules}}{\text{mole}}}{\sqrt{2 \times 8.314473 \frac{\text{J}}{\text{mol} \times \text{K}} \times 298.15 \text{ K} \times \pi \times 0.031998 \frac{\text{kg}}{\text{mol}}}} \\ &= 5.46651 \times 10^{27} \frac{\text{molecules}}{\text{m}^2 \text{ s}} \end{aligned}$$

This is how many molecules strike 1 m² of the surface every second. In order to determine the size of hole required to allow the oxygen molecules to escape at the rate given above, one divides this into the required escape rate:

$$\begin{aligned} A &= \frac{N}{Z_{\text{wall}}} = \frac{3.13664 \times 10^{21} \frac{\text{molecules}}{\text{s}}}{5.46651 \times 10^{27} \frac{\text{molecules}}{\text{m}^2 \times \text{s}}} = 5.73792 \times 10^{-7} \text{ m}^2 \\ &= 5.73792 \times 10^{-3} \text{ cm}^2 \\ &= 0.573792 \text{ mm}^2 \end{aligned}$$

So, this is small orifice, but not unreasonably small. It is certainly of the size that one finds in the jets in burners.

5. (10 point s) . Calculate the work performed by isothermal reversible expansion of 2 moles of nitrogen gas from 1 L to 25 L at room temperature, assuming ideal gas behavior.

$$dU = dq - PdV = 0 \text{ for an ideal gas if the process is isothermal}$$

$$\text{Thus, } dw = -PdV = -\frac{nRT}{V}dV$$

and

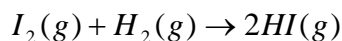
$$\begin{aligned} w &= -\int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \int_{V_1}^{V_2} \frac{1}{V} dV = -nRT \ln \frac{V_2}{V_1} \\ &= -2 \text{ mol} \times 8.314473 \frac{\text{J}}{\text{mol} \times \text{K}} \times 298.15 \text{ K} \times \ln \frac{25}{1} = -15959 \text{ J} = -15.959 \text{ kJ} \end{aligned}$$

The fact that w is negative indicates that q is positive. Therefore, heat must flow **into** the gas to maintain the conditions (constant temperature) to compensate for the work the gas does in expanding against the external pressure applied in a reversible process.

6. (10 points) For each expression given in the left column, chose the appropriate description from the right column

<u>c</u>	(1) $C_{Pm} - C_{Vm} = R$	a) Zero th law of thermodynamics
<u>g</u>	(2) $\sqrt{\frac{3RT}{M}}$	b) Average speed
<u>e</u>	(3) $q = I^2 R t$	c) Heat capacity relationship for ideal gas
<u>l</u>	(4) $dU = dq + dw$	d) The law of Boyle-Mariotte
<u>i</u>	(5) $C_{Vm} = 3R$	e) Joule's law of electrical heating
		f) The law of excessive heat capacity
		g) RMS speed
		h) Heat capacity relationship for any solid
		i) The Law of Dulong and Petit
		j) Sutherland potential
		k) The gravitation law
		l) First law of thermodynamics
		m) Most probable speed
		n) Shomate equation
		o) Heat capacity relationship for any liquid

7. (15 points) For the following gas-phase reaction (with all reactants and products being gases), assume ideal gas behavior to obtain ΔH of this reaction at 400 K.



At 298.15 K, according to Table 5.8, $\Delta H = 2 \text{ mol} \times 26.5 \text{ kJ/mol} - 0 - (1 \text{ mol}) 62.4 \text{ kJ/mol} = -9.4 \text{ kJ}$. [HINT: You may assume that all gases are in the equipartition limit at 298.15 K and at higher temperatures.]

To obtain the ΔH at 400 K, this value should be corrected by adding $\int_{298.15 K}^{400 K} C_{P,m}(\text{prod}) - C_{P,m}(\text{react}) dT$ to the value at 298.15 K.

This is

$$\int_{298.15 K}^{400 K} C_{P,m}(\text{prod}) - C_{P,m}(\text{react}) dT = \int_{298.15 K}^{400 K} 2C_{P,m}(HI(g)) - C_{P,m}(H_2(g)) - C_{P,m}(I_2(g)) dT$$

For any diatomic ideal gas, $C_{P,m} = C_{V,m} + R = \frac{5}{2}R + R = \frac{7}{2}R$ and

$$\int_{298.15 K}^{400 K} 2C_{P,m}(HI(g)) - C_{P,m}(H_2(g)) - C_{P,m}(I_2(g)) dT = \int_{298.15 K}^{400 K} 2 \times \frac{7}{2}R - \frac{7}{2}R - \frac{7}{2}R dT = 0$$

and thus for this reaction, $\Delta H = -9.4 \text{ kJ/mol}$ independent of temperature.

8. (15 points) The temperature dependence of the heat capacity of litharge (a solid lead oxide, PbO) can be expressed well by an abbreviated Shomate equation: $C_{p,m} = 44.35 + 2.47 \times 10^{-3} T$ for temperature expressed in units of K and for the heat capacity in the units of $\text{J mol}^{-1} \text{K}^{-1}$. Although the melting point of this red solid is 888°C , the reaction to obtain it from lead metal is normally run at 600°C , meaning that the oxide is produced in its solid form. Based on the information provided, estimate the heat released upon cooling a mole of litharge from the temperature of the reaction to room temperature at atmospheric pressure.

$$dH = C_p dT + \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP$$

At constant pressure, this expression simplifies to

$$dH = C_p dT \text{ and } \Delta H = q = \int_{T_1}^{T_2} C_p dT$$

$$\begin{aligned} \Delta H &= \int_{600+273.15\text{K}_1}^{298.15\text{K}} C_p dT = \int_{600+273.15\text{K}_1}^{298.15\text{K}} (44.35 + 2.47 \times 10^{-3} T) dT \frac{\text{J}}{\text{mol}} \\ &= 44.35(298.15 - 873.15) \frac{\text{J}}{\text{mol}} + 2.47 \times 10^{-3} \times \frac{T^2}{2} \Big|_{873.15\text{K}}^{298.15\text{K}} \frac{\text{J}}{\text{mol}} \\ &= -25,501 \frac{\text{J}}{\text{mol}} - 832 \frac{\text{J}}{\text{mol}} = -26333 \frac{\text{J}}{\text{mol}} \end{aligned}$$

9. (5 points, extra credit) In a surface process, where the 2D description is appropriate, **derive** the expression for the probability distribution function, assuming that the 1D distribution is exactly the same as in a gas.

In 1D:

$$f(v_x)dv_x = \sqrt{\frac{m}{2\pi kT}} \exp\left(\frac{-mv_x^2}{2kT}\right) dv_x$$

In 2D, the products of such functions look like:

$$F(v_x, v_y)dv_x dv_y = \frac{m}{2\pi kT} \exp\left(\frac{-mv_x^2}{2kT}\right) \exp\left(\frac{-mv_y^2}{2kT}\right) dv_x dv_y$$

Since $v^2 = v_x^2 + v_y^2$,

$$F(v_x, v_y)dv_x dv_y = \frac{m}{2\pi kT} \exp\left(\frac{-mv^2}{2kT}\right) dv_x dv_y$$

To obtain the expression for the speed distribution function, one needs to find the area in a 2D velocity space with speeds between v and $v+dv$:

$Area = \pi(v + dv)^2 - \pi v^2$, which equals $2\pi v dv$, if we neglect terms higher than first order. (You will arrive at the same formula by taking a differential of the area.)

Thus:

$$F(v)dv = \frac{m}{kT} \exp\left(\frac{-mv^2}{2kT}\right) v dv$$