

CHM 3400 – Fundamentals of Physical Chemistry
First Hour Exam

There are five problems on the exam. Do all of the problems. Show your work

$$R = 0.08206 \text{ L}\cdot\text{atm}/\text{mole}\cdot\text{K}$$

$$R = 0.08314 \text{ L}\cdot\text{bar}/\text{mole}\cdot\text{K}$$

$$R = 8.314 \text{ J}/\text{mole}\cdot\text{K}$$

$$N_A = 6.022 \times 10^{23}$$

$$1 \text{ L}\cdot\text{atm} = 101.3 \text{ J}$$

$$1 \text{ atm} = 1.013 \text{ bar} = 1.013 \times 10^5 \text{ N}/\text{m}^2$$

$$1 \text{ atm} = 760 \text{ torr}$$

1. (20 points) A gas mixture contains two gases, neon (Ne, $M = 20.17 \text{ g}/\text{mol}$) and argon (Ar, $M = 39.95 \text{ g}/\text{mol}$). The density of the gas mixture, at $T = 300.0 \text{ K}$, is $\rho = 0.562 \text{ g}/\text{L}$, and the partial pressure of neon in the gas mixture is $p(\text{Ne}) = 328. \text{ torr}$. You can assume ideal gas behavior for the gases in the mixture.

a) Find the mass of neon contained in 1.000 L of the above gas mixture.

b) Find $p(\text{Ar})$, the partial pressure of argon in the above gas mixture. Give your final answer in units of torr.

2. (20 points) In an experiment, $4296. \text{ J}$ of heat is added to a sample of a substance (not an ideal gas). The addition of heat is carried out reversibly and at a constant external pressure $p_{\text{ex}} = 24.10 \text{ atm}$. The temperature of the substance increases from an initial value $T_i = 22.8 \text{ }^\circ\text{C}$ to a final value $T_f = 37.9 \text{ }^\circ\text{C}$. During the process, the volume occupied by the substance increases by 9.8 mL . Based on the above information, find the following:

a) C_p , the average value for the constant pressure heat capacity for the substance over the temperature range of the process carried out above.

b) q , w , ΔU , and ΔH for the process.

3. (20 points) Ammonia (NH_3 , $M = 17.03 \text{ g}/\text{mol}$) is a trace gas in the Earth's atmosphere, and is also found in the atmospheres of other planets and moons.

a) What is the v_{rms} , the rms average speed of an ammonia molecule, at $T = 500.0 \text{ }^\circ\text{C}$?

b) One formula for modeling the temperature dependence of the constant pressure molar heat capacity of a gas has been developed by researchers at NASA. They fit experimental data to a polynomial expression in terms of temperature. For ammonia (NH_3) the equation they use is as follows:

$$C_{p,m}(\text{NH}_3(\text{g})) = a + bT + cT^2 \quad (3.1)$$

For ammonia, the values for the fitting parameters are $a = 24.619 \text{ J}/\text{mol}\cdot\text{K}$, $b = 3.75 \times 10^{-2} \text{ J}/\text{mol}\cdot\text{K}^2$, and $c = -0.138 \times 10^{-5} \text{ J}/\text{mol}\cdot\text{K}^3$. Note that T in eq 3.1 is the absolute temperature (in Kelvin).

Find the values for q , w , ΔU , and ΔH when the temperature of 1.000 mole of ammonia gas changes from an initial value $T_i = 300.0 \text{ K}$ to a final value $T_f = 800.0 \text{ K}$ by a reversible heating of the gas at a constant pressure $p = 5.00 \text{ torr}$. You may assume that for the conditions of pressure and temperature in the problem ammonia obeys the ideal gas law.

4. (20 points) Pyrogallol (1,2,3-trihydroxybenzene, $C_6H_3(OH)_3(s)$) is used in some hair dyes and also in the analysis of the oxygen content of gas samples.

- Give the correctly balanced formation and combustion reaction for pyrogallol.
- Based on the data below, find the value for $\Delta H^\circ_f(C_6H_3(OH)_3(s))$, the enthalpy of formation for pyrogallol.

Combustion data

$$\Delta H^\circ_c(C_6H_3(OH)_3(s)) = - 2672.3 \text{ kJ/mol}$$

Formation data

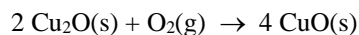
$$\Delta H^\circ_f(CO_2(g)) = - 393.51 \text{ kJ/mol}$$

$$\Delta H^\circ_f(H_2O(l)) = - 285.83 \text{ kJ/mol}$$

5. (20 points) Thermodynamic data for several pure chemical substances are given below (at $T=298.0 \text{ K}$), and may be of use in doing the following problem.

Substance	ΔH°_f (kJ/mol)	ΔG°_f (kJ/mol)	S° (J/mol·K)	$C_{p,m}$ (J/mol·K)
CuO(s)	- 157.3	- 129.7	42.63	42.30
Cu ₂ O(s)	- 168.6	- 146.0	93.14	63.64
O ₂ (g)	0.0	0.0	205.14	29.36

- What are the values for ΔG°_{rxn} , ΔH°_{rxn} , and ΔS°_{rxn} (at $T = 298.0 \text{ K}$) for the following reaction?



- What is the value of S° for CuO(s) at $T = 373. \text{ K}$?

Solutions.

1) a) $pV = nRT$, and so for the neon gas in the mixture

$$(n/V) = \frac{p}{RT} = \frac{(328. \text{ torr})(1 \text{ atm}/760 \text{ torr})}{(0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(300.0 \text{ K})} = 0.01753 \text{ mol Ne/L}$$

and so $\rho(\text{Ne}) = \frac{0.01753 \text{ mol Ne}}{\text{L}} \frac{20.17 \text{ g}}{\text{mol}} = 0.3536 \text{ g Ne/L}$

Therefore, 1.000 L of the gas mixture contains 0.3536 g of neon.

b) $\rho = \rho(\text{Ne}) + \rho(\text{Ar})$, and so $\rho(\text{Ar}) = \rho - \rho(\text{Ne})$

and so $\rho(\text{Ar}) = 0.562 \text{ g/L} - 0.3536 \text{ g/L} = 0.2084 \text{ g Ar/L}$

We can convert this to the number of moles of argon per liter of gas mixture

$$n/V = (0.2084 \text{ g Ar/L}) (1 \text{ mol Ar}/39.95 \text{ g}) = 0.00522 \text{ mol Ar/L}$$

From the ideal gas law

$$p = (n/V)RT = (0.00522 \text{ mol/L}) (0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}) (300.0 \text{ K}) \\ = 0.1284 \text{ atm} (760 \text{ torr}/1 \text{ atm}) = 97.6 \text{ torr}$$

2) a) $C_p = \frac{dq_p}{dT} \cong \frac{q_p}{\Delta T} = \frac{4296 \text{ J}}{(37.9 - 22.8) \text{ }^\circ\text{C}} = 284.5 \text{ J}/^\circ\text{C} = 284.5 \text{ J/K}$

b) The process is constant pressure, and so $q = \Delta H = 4296 \text{ J}$

The process is reversible and at constant pressure, and so

$$w = - \int_i^f p_{\text{ex}} dV = - \int_i^f p dV = - p \int_i^f dV = - p \Delta V \\ = - (24.10 \text{ atm}) (9.8 \times 10^{-3} \text{ L}) = - 0.236 \text{ L}\cdot\text{atm} (101.3 \text{ J/L}\cdot\text{atm}) = - 23.9 \text{ J}$$

Finally, from the first law, $\Delta U = q + w = 4296 \text{ J} + (- 23.9 \text{ J}) = 4272 \text{ J}$

3) a) $v_{\text{rms}} = (3RT/M)^{1/2} = [3 (8.314 \text{ J/mol}\cdot\text{K}) (773.2 \text{ K}) / (17.03 \times 10^{-3} \text{ kg})]^{1/2} = 1064 \text{ m/s}$

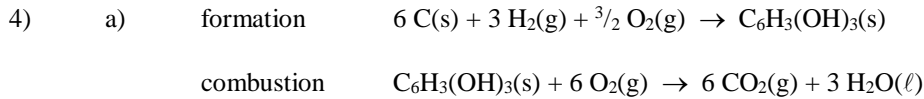
b) The process is the constant pressure reversible heating of a gas, and so

$$q = \Delta H = \int_i^f n C_{p,m} dT = n \int_i^f (a + bT + cT^2) dT \\ = n \{ a (T_f - T_i) + (b/2) (T_f^2 - T_i^2) + (c/3) (T_f^3 - T_i^3) \} \\ = (1.000 \text{ mol}) \{ (24.619 \text{ J/mol}\cdot\text{K}) (800.0 \text{ K} - 300.0 \text{ K}) \\ + (1/2)(3.75 \times 10^{-2} \text{ J/mol}\cdot\text{K}^2) [(800.0 \text{ K})^2 - (300.0 \text{ K})^2] \\ + (1/3) (- 0.138 \times 10^{-5} \text{ J/mol}\cdot\text{K}^3) [(800.0 \text{ K})^3 - (300.0 \text{ K})^3] \} \\ = (1.000 \text{ mol}) \{ (12309.5 \text{ J/mol}) + 10312.5 \text{ J/mol} + (- 223.1 \text{ J/mol}) \} = 22399 \text{ J}$$

Because the gas is ideal, $C_{p,m} - C_{v,m} = R$, or $C_{v,m} = C_{p,m} - R$

$$\begin{aligned} \text{and so } \Delta U &= \int_i^f n C_{v,m} dt = n \int_i^f C_{v,m} dV = n \int_i^f (C_{p,m} - R) dT = \Delta H - nR (T_f - T_i) \\ &= 22399. \text{ J} - (1.000 \text{ mol})(8.314 \text{ J/mol}\cdot\text{K})(800.0 \text{ K} - 300.0 \text{ K}) = 18242. \text{ J} \end{aligned}$$

Finally, from the first law $\Delta U = q + w$, and so $w = \Delta U - q = (18242. \text{ J}) - (22399. \text{ J}) = - 4157 \text{ J}$



b) Using the balanced combustion reaction above and the general expression for the enthalpy change for a chemical reaction, we may say

$$\Delta H^\circ_c(\text{C}_6\text{H}_3\text{(OH)}_3\text{(s)}) = [6 \Delta H^\circ_f(\text{CO}_2\text{(g)}) + 3\Delta H^\circ_f(\text{H}_2\text{O}(\ell))] - [\Delta H^\circ_f(\text{C}_6\text{H}_3\text{(OH)}_3\text{(s)})]$$

or
$$\begin{aligned} \Delta H^\circ_f(\text{C}_6\text{H}_3\text{(OH)}_3\text{(s)}) &= [6 \Delta H^\circ_f(\text{CO}_2\text{(g)}) + 3\Delta H^\circ_f(\text{H}_2\text{O}(\ell))] - [\Delta H^\circ_c(\text{C}_6\text{H}_3\text{(OH)}_3\text{(s)})] \\ &= [6 (- 393.51 \text{ kJ/mol}) + 3 (- 285.83 \text{ kJ/mol})] - (- 2672.3 \text{ kJ/mol}) = - 546.3 \text{ kJ/mol} \end{aligned}$$

5) a)
$$\begin{aligned} \Delta G^\circ_{\text{rxn}} &= [4 \Delta G^\circ_f(\text{CuO(s)})] - [2 \Delta G^\circ_f(\text{Cu}_2\text{O(s)}) + \Delta G^\circ_f(\text{O}_2\text{(g)})] \\ &= [4 (- 129.7)] - [2 (- 146.0) + 1 (0.0)] = - 226.8 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \Delta H^\circ_{\text{rxn}} &= [4 \Delta H^\circ_f(\text{CuO(s)})] - [2 \Delta H^\circ_f(\text{Cu}_2\text{O(s)}) + \Delta H^\circ_f(\text{O}_2\text{(g)})] \\ &= [4 (- 157.3)] - [2 (- 168.6) + 1 (0.0)] = - 292.0 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ_{\text{rxn}} &= [4 S^\circ(\text{CuO(s)})] - [2 S^\circ(\text{Cu}_2\text{O(s)}) + S^\circ(\text{O}_2\text{(g)})] \\ &= [4 (42.63)] - [2 (93.14) + 1 (205.14)] = - 220.90 \text{ J/mol}\cdot\text{K} \end{aligned}$$

b) $S^\circ(\text{CuO(s, 373. K)}) = S^\circ(\text{CuO(s, 298 K)}) + \int_{298}^{373} (C_{p,m}(\text{CuO(s)})/T) dT$

If we assume $C_{p,m}$ is constant over this temperature range, then

$$\begin{aligned} S^\circ(\text{CuO(s, 373. K)}) &= S^\circ(\text{CuO(s, 298 K)}) + C_{p,m}(\text{CuO(s)}) \ln(373/298) \\ &= 42.63 \text{ J/mol}\cdot\text{K} + (42.30 \text{ J/mol}\cdot\text{K}) \ln(373/298) \\ &= 42.63 \text{ J/mol}\cdot\text{K} + 9.50 \text{ J/mol}\cdot\text{K} = 52.13 \text{ J/mol}\cdot\text{K} \end{aligned}$$