Exam I

CH 353 Summer '07

Vanden Bout

Name: KEY

Carefully read all the problems. The exam should have 4 pages of questions. The first page has potentially useful information. The last page is for extra writing space. Problems may have extraneous information.

Potentially useful information

R = 8.314 J K^{-1} mol^{-1} R = 8.314x10^{-2} L bar K^{-1} mol^{-1} R = 8.206x10^{-2} L atm mol^{-1} K^{-1}

1 cal = 4.184 J 1 atm = 1.01325 bar T/K = T/°C + 273.15

1 atm-L = 101.325 J 1 bar-L = 100 J

$$\int \frac{dx}{a+x} = \ln(a+x) \qquad \int \frac{dx}{x^2} = -\frac{1}{x}$$

Van der Waals equation $(P + \frac{a}{V_m^2})(V_m - b) = RT$

$$w = -\int P_{ex} dV$$

$$q = \int C_v dT \qquad q = \int C_P dT$$

$$\Delta U = q + w \qquad H \equiv U + PV$$

Please sign at the bottom to certify that you have worked on your own.

I certify that I have worked the following exam without the help of others, and that the work I am turning in is my own.

Signed: --

Signature Date

1. True/False (10 points each)
Classify the following as either True or False

T F A process is considered thermodynamically reversible if the initial state and final state of the system are the same. cyclic

T F An ideal gas has no intermolecular attractions or repulsions

T F The van der Waals equation of state exactly describes the behavior of a real gas. estimate

T F ΔH is always equal to q only @ const P

T F At a constant pressure of 1 atm, 2000J of heat are used to increase the temperature of an aluminum block. For this process, ΔU of the block will be slightly less than 2000J. slight expansion $w < 0$

$\Delta U = q + w$

2. Short Answer (25 points each)

The Redlich-Kwong (RK) equation of state is given below

$$P = \frac{RT}{V_m - b} - \frac{a}{T^{1/2}V_m(V_m - b)}$$ where a and b are both positive constants

a. Find an equation for the compression factor (Z) of a gas that obeys the RK eq'n of state in **the limit of infinitely high temperature**.

b. In this limit, is the gas dominated by attractive or repulsive forces?

$$\lim_{T\to\infty} P = \frac{RT}{V_m - b} \qquad Z = \frac{PV_m}{RT} = \frac{RT}{V_m - b}\left(\frac{V_m}{RT}\right) = \frac{V_m}{V_m - b}$$

repulsions $Z > 1$

B. It can be shown that

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

For a gas that obeys the van der waals equation of state,

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$ where a and b are positive constants

Do you think the internal energy will increase, decrease, or stay the same for a volume increase at constant temperature. (provide some justification for your answer).

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\partial}{\partial T}\left[\frac{nRT}{V-nb} - \frac{an^2}{V}\right] = \frac{nR}{V-nb}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\cancel{\frac{nR}{V-nb}}\right) - \left[\cancel{\frac{nRT}{V-nb}} - \frac{an^2}{V^2}\right] = \frac{an^2}{V^2}$$

$$\left(\frac{\partial U}{\partial V}\right)_T > 0 \quad \therefore \text{ increase } U \text{ w/ } T\uparrow$$

Benzoic acid ($C_7H_6O_2$) reacts with oxygen by the following reaction

$$C_7H_6O_2(s) + \frac{15}{2}O_2(g) \rightarrow 3H_2O(l) + 7CO_2(g)$$

Substance	$\Delta_f H°$ (kJ mol^{-1})	C_P (J K^{-1} mol^{-1})
$C_7H_6O_2$ (s)	-386	146.8
O_2 (g)	0	29.4
H_2O (l)	-286	75.3
CO_2 (g)	-393.5	37.11

Use the information below to find $\Delta_R H°$ for this reaction at 298K. (data at 298K)

Assuming you start with 1 g of benzoic acid and excess O_2 and the benzoic acid reacts completely at a constant temperature of 298 K and a constant pressure of 1 bar, what are ΔH, ΔU, q, and w?

$$\Delta_R H° = 3\Delta_f H_{H_2O(l)} + 7\Delta_f H_{CO_2} - \frac{15}{2}\cancel{\Delta_f H°_{O_2}} - \Delta_f H°_{BE}$$

$$= 3(-286) + 7(-393.5) - (-386) = -3227 \text{ kJ mol}^{-1}$$

$$\frac{1\text{ g}}{122 \text{ g mol}^{-1}} = 8.20 \cdot 10^{-3} \text{ mol}$$

$$\Delta H = n \times \Delta_R H° = 26.45 \text{ kJ}$$

ΔU = 26.45 kJ

ΔH = -26.45 kJ

w = +10 J

q = -26.45 kJ

$\Delta H = q$ const P

$W = -P\Delta V = -\Delta n RT$

$W = -\left(-\frac{1}{2} \times 8.2 \cdot 10^{-3}\right)(8.314)(298)$

$W = 10$ J

$\Delta U = q + w = 26.45$

4. (50 points)

2 moles of an ideal gas ($C_{V,m}$ = 1.5R) are held in a piston at an initial temperature of 300 K and an initial pressure of 1 bar. You simultaneous increase the external pressure to a constant 4 bar, and change the surrounding temperature to a constant 400 K. The system evolves until it is at both mechanical and thermal equilibrium in a process that is neither isothermal nor adiabatic. What are ΔU, ΔH, w, and q for this process (give your answer in J).

$$C_v = 3R$$

$$\Delta U = C_v \Delta T = 3R(400-300) = 2494\ J$$

$$\Delta H = C_p \Delta T = 5R(100) = 4157\ J$$

$$w = -P_{ex}\Delta V = -P_f(V_f - V_i)$$

$$w = -P_f V_f + \frac{P_f}{P_i} P_i V_i = -nRT_f + 4nRT_i$$

$$w = -(2)(8.314)(400) + 4(2)(8.314)(300)$$

$$w = +13300\ J$$

$$q = \Delta U - w = 2494 - 13300 = -10,810$$

ΔU = 2494 J

ΔH = 4157 J

w = +13,300

q = -10,810 J