Print in upper case the first three letters of your last name here: ☐☐☐

Your name: _____

Chemistry 342

First Exam

September 24, 1999

$1\ J = 1\ kg\ m^2\ s^{-2}$ $k_B = 1.38066\times10^{-23}\ J\ K^{-1}$ $R = N_{Avogadro}k_B$

$R = 8.31441\ J\ mol^{-1}\ K^{-1} = 1.98718\ cal\ mol^{-1}\ K^{-1} = 0.082057\ L\ atm\ mol^{-1}\ K^{-1}$

$p/p_0 = \exp[-(M/RT)gz]$ *barometric formula where* $g = 9.80665\ m\ s^{-2}$

monatomic gas molar heat capacity: $C_V = (3/2)R$

General relations for any equation of state:

$(\partial U/\partial V)_T = T(\partial p/\partial T)_V - p$ $\qquad (\partial H/\partial p)_T = -T(\partial V/\partial T)_p + V$

$C_p - C_V = \{p + (\partial U/\partial V)_T\}(\partial V/\partial T)_p$

1. A monatomic gas obeys the equation of state $pV = nRT + nap$ where $a = 0.02\ L\ mol^{-1}$, such that $(\partial U/\partial V)_T = 0$ for the gas. This gas is taken from state 𝒜 (10. L, 1 atm, T= 304.7 K) to state ℬ (? L, 20 atm, T= 304.7 K) by several possible paths.

Path I : A compression along the isotherm connecting initial and final states.

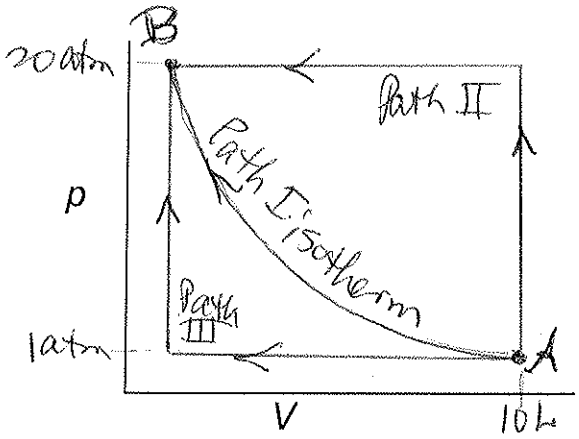
Path II: A constant volume process which takes the gas from the initial pressure to the final pressure, followed by a constant pressure (20 atm) process which takes the gas to the final state.

Path III: A constant pressure (1 atm) process which takes the gas from the initial volume to the final volume, followed by a constant volume process which takes the gas to the final state.

Consider each 𝒜→ℬ path and **calculate** ΔU and ΔH in joules **for each path**.

For each path, calculate q and W where possible (if not, say why not).

First, **draw** these three paths on the pV diagram of the gas:



$V = \frac{nRT}{p} + na$ a is a constant here

$\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p}$

$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V = -T\left(\frac{nR}{p}\right) + \left(\frac{nRT}{p} + na\right)$

$= na$

Given $\left(\frac{\partial U}{\partial V}\right)_T = 0 \therefore C_p - C_V = R$

Find number of moles:

$n = pV/(RT + ap)$

$= 1\ atm\ 10\ L / (0.082057 \times 304.7\ K + 0.02 \times 1\ atm)$

$L\ atm\ mol^{-1}\ K \qquad L\ mol^{-1}$

$n = 0.3996\ mol$

$V_f = 0.3996[0.082057 \times 304.7 + 0.02 \times 20]/20$

$V_f = 0.507\ L$

$n = 0.3996 \text{ mol}$

$V_i = 10 \text{ L}$ $T = 304.7 \text{ K}$

$V_f = 0.507 \text{ L}$ $na = 0.008 \frac{\text{L}}{}$

Path I	Path II	Path III
W along the isotherm means along $P_{op} = nRT/(V-na)$ $dW = -P_{op}dV$ $W = -\int_{V_i}^{V_f} \frac{nRT}{V-na} dV$ $W = -0.3996 \times 0.08205 \times 304.7 \times \ln\left(\frac{V_f - na}{V_i - na}\right)$ $= 30 \text{ Latm}$ $= 3.04 \text{ kJ}$	**W** 2 steps First is $dV = 0$ $\therefore W = 0$ Second is $P_{op} = 20 \text{ atm}$ $W = -\int P_{op} dV$ $= -20 \int_{10}^{0.507} dV$ $W = 190 \text{ Latm}$ $= 19.25 \text{ kJ}$	**W** 2 steps First is $P_{op} = 1 \text{ atm}$ $W = -\int P_{op} dV$ $= -1 \int_{10}^{0.507} dV$ $W = +9.493 \text{ Latm}$ Second is $dV = 0$ $\therefore W = 0$ Total $W = +9.493 \text{ Latm}$ $= 961.9 \text{ J}$
q First law: $\Delta U = q + W$ (from below) $0 = q + 30 \text{ Latm}$ (from below) $\therefore q = -30 \text{ Latm}$ $= -3.04 \text{ kJ}$	**q** First law $\Delta U = q + W$ (from below; from above) $0 = q + 190 \text{ Latm}$ $\therefore q = -190 \text{ Latm}$ $= -19.25 \text{ kJ}$	**q** $\Delta U = q + W$ (from below; from above) $0 = q + 9.493 \text{ Latm}$ $\therefore q = -9.493 \text{ Latm}$
ΔU $dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$ zero; given zero $\therefore \Delta U = 0$	**ΔU** same as path I since ΔU is independent of path since U is a state function $\Delta U = 0$	**ΔU** same ... $\Delta U = 0$
ΔH $dH = C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$ zero; na $\Delta H = \int_{1 \text{ atm}}^{20 \text{ atm}} na \, dp = 0.152 \text{ Latm}$	**ΔH** same as path I since ΔH is independent of path since H is a state function $\Delta H = 0.152 \text{ Latm}$ $= 15.4 \text{ J}$	**ΔH** same ... $\Delta H = 0.152 \text{ Latm}$ $= 15.4 \text{ J}$

or else

$\Delta H = \underbrace{\Delta U}_{\text{zero}} + \underbrace{\Delta(pV)}_{P_f V_f - P_i V_i}$

= same answer

2. The biochemical reactions necessary to sustain life in a person produce about 6000 kJ day^{-1} of heat at constant pressure. This is the basal metabolic rate. Consider one of the large number of reactions that may occur:

$$3O_2(g, 1\ atm) + 2\ glycine(aq.) \rightarrow urea(aq.) + 3CO_2(g, 1\ atm) + 3H_2O(l)$$

Suppose that you have obtained from the data section of your textbook, the following *standard enthalpies of transformation at 298 K in kJ* mol^{-1}:

$\Delta H^{\ominus}$ of oxidation of 1 mol solid glycine to CO_2 , ammonia, and liquid water $= a$

$\Delta H^{\ominus}$ of hydrolysis of 1 mol solid urea to CO_2 and ammonia $= b$

$\Delta H^{\ominus}$ of dissolution of solid glycine $= c$

$\Delta H^{\ominus}$ of dissolution of solid urea $= d$

In case you have forgotten: glycine NH_2CH_2COOH urea H_2NCONH_2
(aq.) means very dilute aqueous solutions

Suppose n moles of urea are produced via this reaction per day, how many kJ day^{-1} is the contribution of this reaction to the metabolic rate?

$2 \cdot \{\frac{3}{2} O_2(g) + NH_2CH_2COOH_{(s)} \rightarrow 2CO_{2(g)} + NH_{3(g)} + H_2O_{(l)}\ \Delta H^{\ominus} = a\}$

$-1 \cdot \{H_2O_{(l)} + H_2NCONH_{2(s)} \rightarrow 1CO_{2(g)} + 2NH_{3(g)}\ \Delta H^{\ominus} = b\}$

$-2 \cdot \{NH_2CH_2COOH_{(s)} \rightarrow NH_2CH_2COOH_{(aq)}\ \Delta H^{\ominus} = c\}$

$+1 \cdot \{H_2NCONH_{2(s)} \rightarrow H_2NCONH_{2(aq)}\ \Delta H^{\ominus} = d\}$

$3O_{2(g)} + 2\ glycine_{(aq)} \rightarrow urea_{(aq)} + 3CO_{2(g)} + 3H_2O_{(l)}$

$\Delta H^{\ominus} = 2a - b - 2c + d \quad kJ\ mol^{-1}$

for n moles of urea produced per day

$\Delta H = n(2a - b - 2c + d)\ kJ\ day^{-1}$ ANSWER

3. If two gases A and B of molecular weight x and y (g mol^{-1}) respectively are found at equal abundance in the atmosphere at sea level, at what height should we expect to find gas A to be three times as abundant as gas B? You may assume that the atmosphere is isothermal at 298 K.

Let Z = height

$P_A/P_{A0} = \exp\left[-\frac{x}{RT} g Z\right]$ $\quad P_B/P_{B0} = \exp\left[-\frac{y}{RT} g Z\right]$

$\ln P_A/P_{A0} = -\left(\frac{x}{RT}\right) g Z$ $\quad \ln P_B/P_{B0} = -(y/RT) g Z$

$\ln P_A/P_{A0} - \ln P_B/P_{B0} = -\left[\frac{x-y}{RT}\right] g Z$

$P_{A0} = P_{B0}$ ← given

$\ln(P_A/P_B) = \ln(3) = 1.0986 = -\frac{[x-y]}{RT} g Z = -[x-y]\,g\,mol^{-1} \times 10^{-3}\,kg/g \times 9.806\,ms^{-2} \times Z_m \,/\, 8.3145\,J\,mol^{-1}\,K^{-1} \times 298\,K$

$\therefore Z(\text{meters}) = \frac{1.0986 \times 8.3144 \times 298}{9.806 \times 10^{-3}\,(y-x)}$ ANSWER

4. If a compound is burned under adiabatic conditions so that all the heat evolved is used in heating the product gases, the maximum temperature reached is called the adiabatic flame temperature. **Calculate this temperature** for the burning of acetylene (ethyne) in oxygen sufficient for complete combustion to CO_2 and $H_2O(g)$. **Predict**: Do you expect the flame temperature of an oxyacetylene torch to be higher or lower when excess oxygen is used?

For ease of calculations, assume independent of temperature the following data:

	C_p J mol^{-1} K^{-1}	C_V J mol^{-1} K^{-1}
$H_2(g)$	28.824	20.5
$O_2(g)$	29.355	21.0
$H_2O(g)$	33.58	25.3
$H_2O(l)$	75.291	75.2
$CO_2(g)$	37.11	28.8
HCCH(g)	43.93	35.0

Also, you may use the following values at 298 K

$\Delta_f H^\ominus$ for the formation of	$\Delta_f H^\ominus$ kJ mol^{-1}
$H_2O(g)$	-241.82
$H_2O(l)$	-285.83
$CO_2(g)$	-393.51
HCCH(g)	+226.73

and at 373 K

$\Delta_{vap} H^\ominus$ for H_2O kJ mol^{-1}
40.656

	initial			final
Reaction	$HCCH(g)$	$+\frac{5}{2}O_2(g)$	$\rightarrow$	$2CO_2(g) + H_2O(g, T_f)$
	298K	298K		T_f
	1 mole	sufficient		$q_p = 0$

H is a state function

$$HCCH(g,298) + \tfrac{5}{2}O_2(g,298) \rightarrow 2CO_2(g,298) + H_2O(l,298)$$

$$\Delta H^\ominus_{298} = 2(\Delta_f H^\ominus CO_2\, g) + 1(\Delta_f H^\ominus H_2O\, l) - 1(\Delta_f H^\ominus HCCH\, g)$$
$$= 2(-393.51) + 1(-285.83) - 1(226.73)$$
$$= -1299.58 \times 10^3\ J$$

$$H_2O(l,298) \rightarrow H_2O(l,373) \quad \Delta H = \int_{298}^{373} C_p dT \quad \text{since } dp = 0$$
$$= 75.291(373-298)$$

$$H_2O(l,373) \rightarrow H_2O(g,373) \quad \Delta_{vap}H = 40.656 \times 10^3\ J$$

$$H_2O(g,373) \rightarrow H_2O(g,T_f) \quad \Delta H = \int_{373}^{T_f} C_p dT$$
$$= 33.58(T_f - 373)$$

$$2CO_2(g,298) \rightarrow 2CO_2(g,T_f) \quad \Delta H = 2 \times 37.11(T_f - 298)$$

---

add them up to get

$$HCCH(g,298) + \tfrac{5}{2}O_2(g,298) \rightarrow 2CO_2(g,T_f) + H_2O(g,T_f)$$

$q_p = 0$ given $\therefore \Delta H = 0$

$$0 = -1299.58 \times 10^3 + 75.291(373-298) + 40.656 \times 10^3 + 33.58(T_f - 373) + 2 \times 37.11(T_f - 298)$$

Solve for T_f

$T_f = 1194.7\ K$ ANSWER

6. Ten moles of nitrogen at 300 K are held by a piston under 40 atm pressure. The pressure is suddenly released to 10 atm and then the gas expands adiabatically. If C_V for N_2 is assumed to be constant and equal to 20.8 J mol^{-1} K^{-1}, calculate the final temperature of the gas. Assume the gas is ideal. Calculate ΔU and ΔH for the change in the gas.

10 mol N_2
$P = 40$ atm
300 K
$V_i = \frac{10 R 300}{40}$

adiabatic →

$P_{op} = 10$ atm

$T_f = ?$
$P = 10$ atm
$V_f = \frac{10 R T_f}{10}$

$dW = -P_{op} dV$

$W = -10 \int_{V_i}^{V_f} dV = -10 \text{ atm} \left[\frac{10 R T_f}{10 \text{ atm}} - \frac{10 R 300}{40} \right] = (-10 T_f + 750) R$

adiabatic $\therefore q = 0$

$\Delta U = q + W = W$

$\Delta U = 10 \times 20.8 (T_f - 300)$ (from below)

$= (-10 T_f + 750) 8.3144$

Solve for T_f, $T_f = 235.75$ K ANSWER

ΔU ideal gas $\left(\frac{\partial U}{\partial V}\right)_T = 0$

$dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$ (zero)

$\Delta U = \int_{300}^{T_f} C_V dT = 10 \text{ mol} \times 20.8 \text{ J mol}^{-1} \text{ K}^{-1} (T_f - 300)$

get T_f from above

$\Delta U = -13364$ J ANSWER

ΔH ideal gas $\left(\frac{\partial H}{\partial P}\right)_T = 0$

$dH = C_p dT + \left(\frac{\partial H}{\partial P}\right)_T dP$ (zero)

$\Delta H = \int_{300}^{T_f} C_p dT$

$= 10 \text{ mol} (20.8 + 8.314)(T_f - 300)$ J mol^{-1} K^{-1}

use T_f from above

$\Delta H = -18706$ J ANSWER