Chemistry 342
September 25, 1998
First Exam **Answers**

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*
$C_p - C_V = \{p + (\partial U/\partial V)_T\}(\partial V/\partial T)_p$ $(\partial H/\partial p)_T = [p + (\partial U/\partial V)_T](\partial V/\partial p)_T + V$
$\mu_{JT} = (\partial T/\partial p)_H$ $(\partial H/\partial p)_T = -C_p\,\mu_{JT}$
monatomic gas molar heat capacity: $C_V = (3/2)R$

1. Investigate some of the technicalities of ballooning using the perfect gas law. Suppose your balloon has a capacity of 10^3 m^3 is filled with He at 20°C and 1 atm pressure. Assume that the volume of the baloon is constant, the atmosphere isothermal at 20°C [293 K] and the molecular weight of air is 28.8 and the ground level pressure is 1 atm. The balloon itself is made of material whose mass may be neglected compared to the load.

(a) What is the density of air at ground level? use ideal gas law

$$\rho_{air} = \left(\frac{P}{RT}\right)M = \frac{1\text{ atm } 28.8\text{ g mol}^{-1}}{0.082057\text{ L atm mol}^{-1}\text{K}^{-1}\ 293\text{K}} = 1.197\text{ g/L}$$

(b) What is the load that the balloon can lift at ground level? [Hint: Archimedes]

The balloon can lift a load because the He balloon displaces an equal VOLUME of air, but itself has a much smaller mass.

$$m_{He} + m_{LOAD} = m_{displaced\ air}$$

$\therefore m_{LOAD} = V(\rho_{air} - \rho_{He})$. At ground level $p = 1$ atm, $\rho_{He} = \left(\frac{P}{RT}\right)M = \frac{(1)(4)}{(.082057)(293)} = 0.166\text{ g/L}$

$$\therefore m_{LOAD} = 10^3\text{ m}^3\left(\frac{100\text{ cm}}{1\text{ m}}\right)^3\left(\frac{1\text{ L}}{10^3\text{ cm}^3}\right)(1.197 - 0.166) = 10^6\text{ L}\,(1.197-0.166)\text{ g/L} = 1.031\times10^6\text{ g}$$

(c) If the balloon is loaded with 80% of the load that it can lift at ground level, at what height will the balloon come to rest?

$$m_{He} + m_{Load} = m_{displaced\ air}$$

$$10^6(0.166) + 0.80(1.031\times10^6) = 10^6(1.197\ \rho/\rho_0)$$

(ρ/ρ_0 = density of air at height Z)

$$\therefore \rho/\rho_0 = 0.8277 = e^{-\frac{MgZ}{RT}}$$

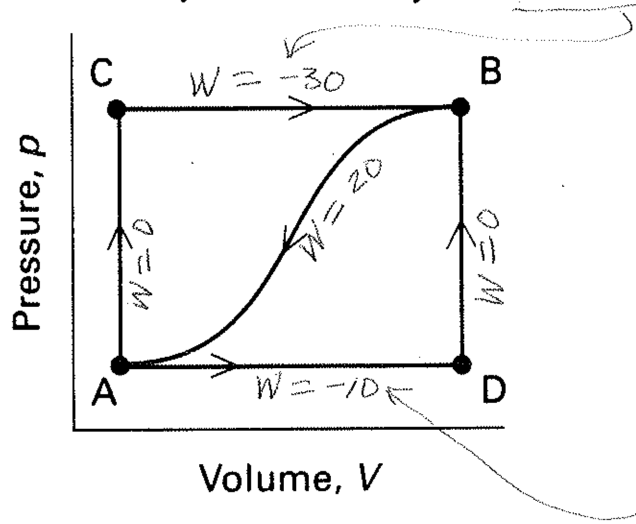
$$\ln 0.8277 = -1.1586\times10^{-4} = -\frac{MgZ}{RT} = \frac{-28.8\times10^{-3}\text{ kg mol}^{-1}\ 9.80\text{ m s}^{-2}\ Z(\text{meters})}{8.3144\text{ J mol}^{-1}\text{K}^{-1}\ 293\text{ K}}$$

$$\therefore Z = 1.632\times10^3\text{ meters}$$

[Note: if we could NEGLECT the mass of the He, then the answer is very simple: $0.80 = \rho/\rho_0$

2. When a system is taken from state A to state B along the path ACB in the figure below, 80 J of heat flows into the system and the system does 30 J of work.

Use First Law in each case



(a) How much heat flows into the system along path ADB if the work done is 10 J?

Given $q_{ACB} = 80$ and $W_{ACB} = -30$
$\therefore U_B - U_A = q_{ACB} + W_{ACB} = 80 - 30 = 50 = q_{ADB} + W_{ADB}$ (since U is a state function) $= q_{ADB} - 10$
$\therefore q_{ADB} = 60$ J ($= q_{AD} + q_{DB}$, of course)

(b) When the system is returned from state B to A along the curved path, the work done on the system is 20 J. Does the system absorb or liberate heat, and how much?

From (a) $U_A - U_B = -50 = q_{A \leftarrow B} + W_{A \leftarrow B} = q_{A \leftarrow B} + 20$ (since U is a state function)
$\therefore q_{A \leftarrow B} = -70$ J

The system liberates heat to the surroundings

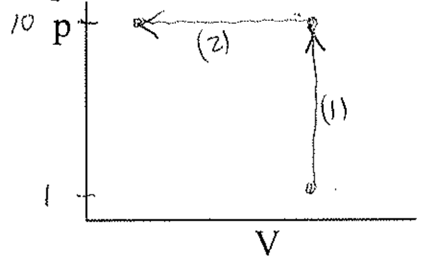
(c) If U_D-U_A = +40 J, find the heat absorbed in each of the processes AD and DB.

(Given) $U_D - U_A = +40 = q_{AD} + W_{AD}$ But $W_{AD} = -10$ since $W_{ADB} = -10$ and $W_{DB} = 0$
$\therefore q_{AD} = +50$ J
Also from (a), $q_{AD} + q_{DB} = 60$ J $\therefore q_{DB} = 10$ J

$\therefore C_p - C_v = R$

3. Assume that air behaves as an ideal gas with $C_p = (7/2)R$. $C_v = \frac{5}{2}R$

(a) In one experiment 1.00 mole of "air molecules" is compressed from 1.00 atm to 10.0 atm at 25°C by the following reversible process: (1) heating at constant volume to the final pressure, followed by (2) cooling at constant pressure to 25°C. Sketch these processes on a pV diagram.



(Initial)$_1$	(Final)$_1$ & (Initial)$_2$	(Final)$_2$
$P_1 = 1$ atm	$P = 10$ atm	$P = 10$ atm
$T = 298$ K	$T = ? = \frac{10 R\, 298}{R} = 2980$ K	$T = 298$ K
$V = \frac{R\, 298}{1} = 24.45$	$V = \frac{R\, 298}{1} = 24.45$	$V = \frac{R\, 298}{10} = 2.445$

Calculate ΔU, ΔH, q, and W, in kJ for each step in the process and for the overall process.

step 1 constant vol.	step 2 constant p	overall sum step 1 + 2
$q = q_V = \int_{298}^{2980} C_v dT$ $= \frac{5}{2} 8.314 [2980 - 298]$ $= 55.748$ kJ	$q = q_P = \int_{2980}^{298} C_p dT$ $= \frac{7}{2} 8.3144 [298 - 2980]$ $= -78.047$ kJ	q $55.748 - 78.047$ $= -22.3$ kJ
$W = \int -P_{op} dV$, $dV = 0$ $\therefore W = 0$	W get from $W = \Delta U - q$ $= -55.748$ $- -78.047$ $= +22.3$ kJ	W $= 0 + 22.3$ kJ $= 22.3$ kJ
ΔU $dU = C_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV$ (zero) $\Delta U = q_V = 55.748$ kJ	ΔU $dU = C_v dT + 0$ $\Delta U = \frac{5}{2} 8.3144 [298 - 2980]$ $= -55.748$ kJ	$\Delta U = 0$ since back to same temperature (298 K) and ideal
ΔH $dH = C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$ (zero) $\Delta H = \frac{7}{2} 8.3144 [2980 - 298]$ $= 78.047$ kJ	ΔH $dH = C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$ (zero) $\Delta H = \frac{7}{2} 8.3144 [298 - 2980]$ $= -78.047$ kJ	$\Delta H = 0$ since ... (same as above)

4. n moles of a gas obeying the equation of state $p(V-nb) = nRT$ ($b = 10^{-1}$ L mol^{-1}) and has $(\partial U/\partial V)_T = 0$, $(\partial H/\partial p)_T = -b$ is subjected to an isothermal reversible expansion from an initial volume of 1.00 L to 24.8 L at 298 K. Calculate the values of ΔU, ΔH, q, and W, in kJ (in terms of n).

q get from $q = \Delta H - W$ $= -W$	W reversible $P_{op} = P_{gas}$ $W = \int dW = -\int P_{op} dV = -nR\,298 \int_{1.0L}^{24.8L} \frac{dV}{V-nb}$ $W = -nR\,298 \ln\left(\frac{24.8-0.1n}{1.0-0.1n}\right)$
ΔU $dU = C_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV$ (zero given) $dT = 0$ $\therefore \Delta U = 0$	ΔH $dH = C_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp$ $dT = 0$; $-b$ given $\Delta H = \int \left(\frac{\partial H}{\partial p}\right)_T dp = -b \int_{p = \frac{nR298}{1.0-0.1n}}^{p = \frac{nR298}{24.8-0.1n}} dp$ $= -b\, nR298 \left[\frac{1}{24.8-0.1n} - \frac{1}{1.0-0.1n}\right]$

5. Calculate the standard enthalpy of formation $\Delta_f H^\ominus$ of $KClO_3$ from the enthalpy of formation of KCl (-436.75 kJ mol^{-1}) together with the following information all at 298 K:

$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$ $\qquad \Delta H^\ominus = -89.4$ kJ mol^{-1}

$\Delta_f H^\ominus$ elements $= 0$

$-89.4 \text{ kJ mol}^{-1} = 2\times(-436.75) + 3\times 0 - 2\Delta_f H_{KClO_3}$

$\Delta_f H^\ominus_{KClO_3} = \frac{2(-436.75)+89.4}{2} = -392.05 \text{ kJ mol}^{-1}$

6. A cylindrical container of fixed total volume is divided into three sections, S_1, S_2, and S_3. The sections S_1 and S_2 are separated by an adiabatic piston, whereas S_2 and S_3 are separated by a diathermic (heat conducting) piston. The pistons can slide along the walls of the cylinder without friction. Each section of the cylinder contains 1.00 mole of a perfect diatomic gas [$C_V = (5/2)R$]. Initially the gas pressure in all three sections is 1.00 atm and the temperature is 298 K. The gas in S_1 is heated slowly until the temperature of the gas in S_3 reaches 348 K.

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Find the final temperature, pressure, and volume, as well as the change in internal energy for each section.

S_1	S_2	S_3
p_f	p_f	p_f
V_f	V_f	V_f
T_f	T_f	T_f
ΔU	ΔU	ΔU

Determine the total energy supplied to the gas in S_1.

S_1	S_2	S_3

Initial: p_1 = 1atm $\quad$ p_2 = 1atm $\quad$ p_3 = 1atm

T_1 = 298 K $\quad$ T_2 = 298 K $\quad$ T_3 = 298 K

ideal: V_1=?=298R/1=24.4 L $\quad$ V_2=?=298R/1=24.4 L $\quad$ V_3=?=298R/1=24.4 L

Since fixed total volume, total work = 0, $W_1 + W_2 + W_3 = 0$

Since adiabatic piston between S_1 and S_2, $\quad q_2+q_3 = 0$

Since pistons are free to slide, then final $p_{f1} = p_{f2} = p_{f3} = p_f$

Since diathermic piston between S_2 and S_3, then T_{f2} is same as T_{f3} = 348 K

Since S_2 and S_3 are at same final p_f and T_f then $V_{f2} = V_{f3}$

What can we calculate?

$dU = C_V dT + (\partial U/\partial V)_T dV$ but $(\partial U/\partial V)_T = 0$ for an ideal gas. Therefore,

$\Delta U_2 = C_V[348 - 298] = (5/2)R[348 - 298] = 250$ cal

$\Delta U_3 = C_V[348 - 298] = (5/2)R[348 - 298] = 250$ cal

First law: $\Delta U_2 = q_2 + W_2$ and $\Delta U_3 = q_3 + W_3$

But since $q_2+q_3 = 0$ and $W_1 + W_2 + W_3 = 0$, then

$$W_1 = -(W_2+W_3) = -(\Delta U_2 + \Delta U_3) = -(250+250) = -500 \text{ cal}$$

Ideal gases in S_2 and S_3 together went through an adiabatic reversible (infinitely slowly) compression brought about by expansion of S_1.

Therefore, $\ln\{[T_{f2}/T_2]^{Cv/R}\} = \ln[V_2/V_{f2}]$ holds.

$\ln\{[348/298]^{5/2}\} = \ln[298R/V_{f2}]$, solve for V_{f2} =16.59 L =V_{f3}

Now ideal gas equation gives p_f from T_{f2} and V_{f2}: $p_f = R(348)/V_{f2}$ =1.72 atm

Now we know also that fixed total volume is the same as total initial volume,

$V_{f1} + 2V_{f2} = 3 \cdot R298/1$, solve for V_{f1}, V_{f1} = 40.16 L

In S_1 we know p_f and V_{f1}, apply ideal gas law: $p_f V_{f1} = R(T_{f1})$, solve for T_{f1}

T_{f1} = 1.72 atm(40.16 L) /.082057 = 841.8 K

In S_1 can now apply First Law: $\Delta U_1 = C_V[T_{f1} - 298] = \ldots = q_1 + W_1$, solve for q_1

(5/2)R[841.8 - 298] = 2701.6 cal = q_1 - *500 cal*, $\quad q_1$ = 3202 cal which is the total energy supplied to the gas in S_1.

S_1	S_2	S_3
p_f 1.72 atm	p_f 1.72 atm	p_f 1.72 atm
V_f 40.16 L	V_f 16.59 L	V_f 16.59 L
T_f 841.8 K	T_f 348 K	T_f 348 K
ΔU 2701.6 cal	ΔU 250 cal	ΔU 250 cal

The total energy supplied to the gas in S_1= 3202 cal