Chemistry Lab

Princeton Science Olympiad Invitational

February 4th, 2017

Written by Reilly Bova '20

Team Name: ________________________ Team Number: _______

Team Members: ____

____

For Official Use Only

Score: __________% Rank: ________

Clean Lab: ☐ YES ☐ NO (-5%)

Post-Test Survey

How would you rate the quality of the lab section?

(Poor) 1 2 3 4 5 (Excellent)

How would you rate the quality of the theoretical questions?

(Poor) 1 2 3 4 5 (Excellent)

How would you rate the difficulty of this test?

(Easy) 1 2 3 4 5 (Hard)

How would you rate the overall quality of this test?

(Poor) 1 2 3 4 5 (Excellent)

Estimate your score on this test: _____ %

(Optional) What material on this test surprised you?

____

____

____

(Optional) What material did this test fail to cover?

____

____

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(Optional) Additional Comments:

____

____

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General Directions

- You have **50 minutes** to complete 1 lab and 6 theoretical problems. A **5-minute warning** will be given. Both the difficulty and the weighting of the theoretical problems increases as you progress.
- **Leave at least 10 minutes** before time is called to clean up your lab. If your lab space when time is called does not resemble the lab space you started with, you will receive a **5% penalty**.
- Do not open the test until you are instructed to begin.
- Write relevant calculations in the appropriate boxes when necessary. **If you want partial credit, you must show your work**.
- **Don't forget units!** Correct answers without units (or with improper units) will not receive full credit.
- If you take the pages of the test apart, make sure to **label each page** with your team number and staple all the pages together (in order) before turning your test in.
- Unless stated otherwise, ΔG, ΔH, and ΔS are per mole.
- In the event of a tie, the percent error of the experimental ΔH and ΔS values calculated in 1.e will be used as tie-breakers.
- This exam is 31 pages long. You will not finish. Best of luck! ☺

Avogadro's Constant	$N_A = 6.0221 \times 10^{23}$ mol^{-1}
Universal Gas Constant	$R = 8.3145$ J·K^{-1}·mol^{-1} = 0.08206 L·atm·K^{-1}·mol^{-1}
Atmospheric Pressure	1 atm = 1.013×10^5 Pa = 760 mmHg
Absolute Zero	0 K = – 273.15°C

PERIODIC TABLE OF THE ELEMENTS

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 **H** 1.008																	2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.61	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57 **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.8	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** (226)	89 **Ac** (227)	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (263)	107 **Bh** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Ds** (281)	111 **Rg** (272)	112 **Cn** (285)	113 (Uut) (284)	114 (Uuq) (289)	115 (Uup) (288)	116 (Uuh) (293)	117 (Uus) (294)	118 (Uuo) (294)

58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)

a	b	c	d	e	f	g	h	i	j	Total	
8	2	8	2	16	5	3	8	3	3	58	35%

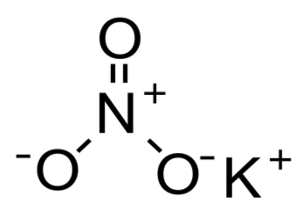
PROBLEM 1
35% of total

Part I – Lab

INTRODUCTION

Potassium nitrate (KNO_3) is an ionic salt that is often found in fertilizer, food preservatives, gunpowder, and fireworks. In an equilibrated, saturated solution of potassium nitrate, the rate of dissolution of the salt into its constituent ions is equal to the rate at which the potassium nitrate crystallizes. The equilibrium constant for this relationship is given by the "solubility product constant" (K_{sp}), which is equivalent to the product of the concentration of ions in the solution. The chemical equation for the dissolution of potassium nitrate in a saturated solution is given by:

$$KNO_{3(s)} \rightleftharpoons K^{+}_{(aq)} + NO3^{-}_{(aq)}$$



Your task is to *determine the thermodynamic variables ΔH, ΔS, & ΔG for the dissolution of potassium nitrate*.

To simplify your calculations, you may assume that the temperature at which the crystals become visible is the precise temperature at which equilibrium is established, and you may disregard the activities of the ions and the ionic strength of the solutions.

MATERIALS

- KNO_3
- Hot Plate
- Stirring Rod
- Large Beaker
- 50 mL Graduated Cylinder
- 10 mL Graduated Cylinder
- Thermometer
- Wash Bottle with DI water
- Ring Stand
- Paper Towels

A MESSY WORKSPACE WHEN TIME IS CALLED WILL RESULT IN A <u>5% Penalty</u>!

PROCEDURE

1. Assemble a hot water bath using the large beaker and the hot plate. You may heat the water, but do not let it boil.

2. Measure about **20** grams of KNO_3 on a balance (**record the exact mass**) and transfer the sample to the 50 mL graduated cylinder.

3. Use the 10 mL graduated cylinder to add a total of about **15** mL of DI water into the 50 mL graduated cylinder (measure 8 mL, and then 7 mL).

4. Secure the 50 mL graduated cylinder such that the sample is submerged in the hot water bath and the thermometer is in turn submerged in the sample. Heat the sample in the hot water until all the KNO_3 is dissolved. The stirring rod may be used to facilitate dissolution, but do not use the thermometer to stir.

5. Once the KNO_3 sample is entirely dissolved, carefully raise the 50 mL cylinder up and out of the hot water bath. Remove the stirring rod and adjust the thermometer such that no part of it is in the solution (i.e. no displacement) while keeping it deep enough inside of the graduated cylinder so that the thermometer does not lose much heat. **Record the exact volume of the solution.** If you are unable to see your sample clearly from the outside of the cylinder, quickly wipe down the cylinder's exterior with a paper towel.

6. Return the thermometer to the solution and watch the solution until the first white crystal appears. **Record the temperature at this moment**.

7. Using the 10 mL graduated cylinder, add about **5** mL of DI water to your solution and return the 50 mL cylinder to the hot water bath, Repeat steps 4 through 6 **five more** times (until the solution is around 40 mL), giving you data for 6 trials.

DATA

Mass KNO_3 (g)			
Trial	Volume of Water (mL)	[KNO_3] (M)	**a)** Crystal Temperature (°C)
1			
2			
3			
4			
5			
6			

b) Write the K_{sp} value in terms of potassium nitrate concentration ($[KNO_3]$).

K_{sp} = __________

Calculations

c) The relationship between free energy (ΔG) and the equilibrium constant (K) for a chemical reaction at a specific temperature (T) is:

$$\Delta G = -R \cdot T \cdot \ln K$$

Use this equation, along with your data, to fill out the table below.

Trial	K_{sp}	$\ln K_{sp}$	Temperature (K)	ΔG ($kJ \cdot mol^{-1}$)
1				
2				
3				
4				
5				
6				

d) The relationship between free energy (ΔG) and enthalpy (ΔH) & entropy (ΔS) for a chemical reaction at a specific temperature (T) is:

$$\Delta G = \Delta H - T \cdot \Delta S$$

Combine this with the equation from part (c) to find an equation in $y = mx + b$ form, where the slope (m) is ($-\Delta H°/R$). Box your answer.

e) Use this equation and six data points (three pairs) to estimate ΔH and ΔS.

Calculation 1 – (between trial __ and __):	Calculation 2 – (between trial __ and __):	Calculation 3 – (between trial __ and __):

Accepted ΔH = ___________	Accepted ΔS = ___________

f) Is ΔG endergonic or exergonic at room temperature (25°C)?

Endergonic	Exergonic

Is ΔH endothermic or exothermic?

Endothermic	Exothermic

Is ΔS negative or positive?

Negative	Positive

Why is this so?

Part II – Related Application

Sodium tetraborate decahydrate ("borax") dissociates in water to form sodium and borate ions and water molecules:

$$Na_2B_4O_7 \cdot 10\ H_2O_{(s)} \rightleftharpoons 2Na^+_{(aq)} + B_4O_5(OH)_4^{2-}{}_{(aq)} + 8H_2O_{(l)}$$

Since borate acts as a base, its concentration can easily be determined by a simple acid-base titration:

$$B_4O_5(OH)_4^{2-} + 2H^+ + 3H_2O \rightleftharpoons 4B(OH)_3$$

g) Write the K_{sp} value for the dissolution of Borax in terms of Borate concentration.

K_{sp} = ________________

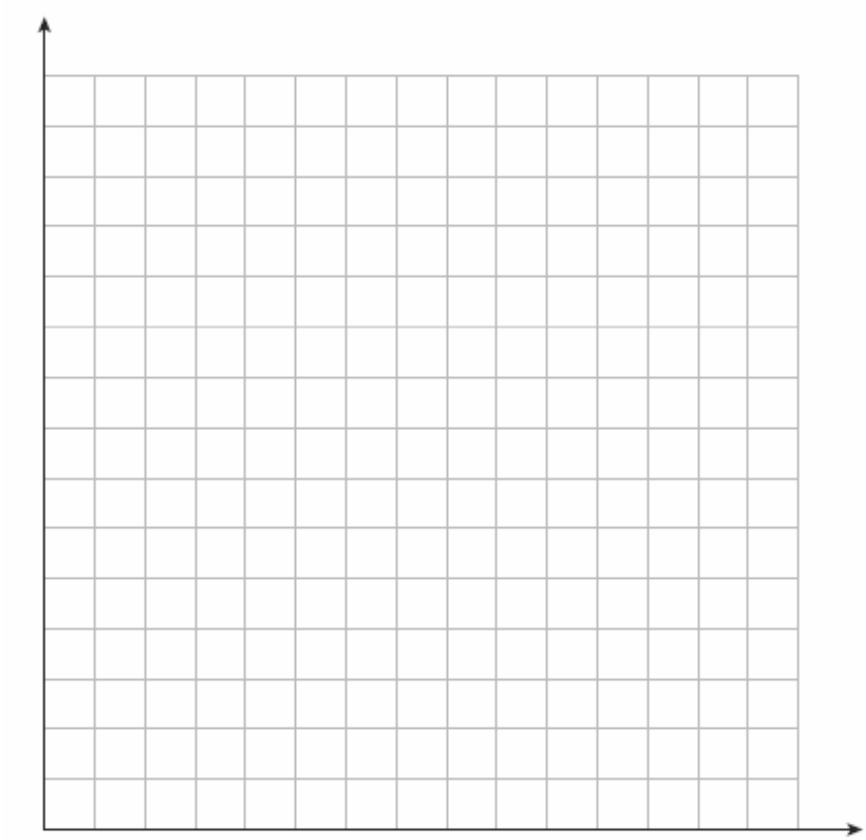
h) A student named Dell Tagee prepared 5.00 mL of borax solution at 45.81°C. She diluted the solution in a flask and titrated it to an endpoint with 49.51 mL of 0.500 M HCl. Calculate ΔG.

ΔG = ______________

i) The literature values of enthalpy and entropy for the dissolution of borax are 110 kJ·mol^{-1} and 380 J·mol^{-1} respectively. Determine the Dell's percent error.

Percent Error: ________%

j) On the set of axes below, sketch a graph with a constant slope of –ΔH/R, where the axes are labeled in terms of T and borate ion concentration. You do not need to mark specific values.



REMEMBER TO LEAVE TIME TO CLEAN UP YOUR LAB!

a	b	c	d	e	f	g	h	Total	
2	2	2	4	3	5	3	2	23	8%

PROBLEM 2
8% of total

a) Stacy Puft places a marshmallow in a closed container and slowly evacuates the air from the chamber. Initially, the marshmallow expands because the air inside of it is trapped; however, the increased surface area of the enlarged marshmallow stretches its (sealing) outer layer until it is porous enough such that internal air can escape, at which point the marshmallow stops expanding because its internal pressure equilibrates with low pressure of the container. When Stacy observes that her marshmallow has stopped expanding, she returns the pressure of the container to normal (its initial state). How does the size of the marshmallow at the end of Stacy's experiment compare to its size at the beginning?

Smaller	Same	Larger

b) Which of the following gases is responsible for the depletion of the ozone layer?

CH_3F	CO_2	CCl_3F	CF_4	NO2

c) Which equation properly models the relationship between a liquid's volume *V*, vapor pressure *P*°, and temperature *T* in a closed container, where *A* and *C* are some arbitrary constants and Δ*H* is the heat of vaporization for the liquid?

$P°\cdot V = n\cdot R\cdot T$	$A\cdot P° = \Delta H\cdot V/(R\cdot T) + C$	$\ln(P°) = A\cdot\Delta H/(R\cdot T)$	$\ln(P°) = C - \Delta H/(R\cdot T)$

d) The volume of a diatomic ideal gas is adiabatically decreased from 2.00 L to 1.00 L. For adiabatic compression of a diatomic gas, the volume raised to seven-fifths and multiplied by the pressure is always equal to some constant ($P\cdot V^{7/5}$ = constant). The initial pressure is 1.54 atm, and the initial temperature is 25.00°C. Calculate the final temperature of the gas.

Temperature (K): ________________

e) What is the average molecular velocity of O_2 gas at STP?

Velocity (m/s): ________________

f) Label the following statements true or false.

Temperature (T) is a state variable	True	False
Heat (Q) is a state variable	True	False
Work (W) is a state variable	True	False
Entropy (ΔS) is a state variable	True	False
Internal Energy (E_{int}) is a state variable	True	False

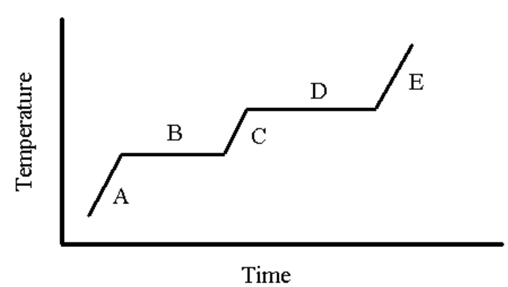
g) Which of the following reversible processes converts all the heat added to a system into work?

Isothermal	Isochoric	Isobaric	Adiabatic	Such a process would violate the 2nd law of thermodynamics

h) Use the phase diagram (for some arbitrary substance) on the right to answer the next two questions.

Which section on the graph can be modeled by the enthalpy of formation of the substance?

A	B	C	D	E



If heat was added at a constant rate for this diagram, could this substance have been water?

Yes	No

a	b	c	d	e	f	g	Total	
9	4	6	10	4	8	4	45	9%

PROBLEM 3
9% of total

Consider a closed 20.0 L flask that contains 20.0 g of hydrogen and 128. g of oxygen at 200°C.

a) Calculate the total pressure of the flask, as well as the partial pressures of hydrogen and oxygen.

P_{H2} = ______________	P_{O2} = ______________	P_{total} = ______________

b) If a spark ignites this mixture of gases, the gases will combust to form water. Write the combustion reaction that would occur. Make sure to include states.

c) Determine how many moles of each product/reactant occupy the flask after the combustion of the mixture is complete.

H_2 (mol) = ______________	H_2 (mol) = ______________	H_2O (mol) = ______________

d) The ΔH°_f for steam is –241.818 kJ·mol^{-1}. The heat capacity of steam is 71.73 J·mol^{-1}, the heat capacity of oxygen gas is 30.59 J·mol^{-1}, and the heat capacity of hydrogen gas is 29.00 J·mol^{-1}. Calculate the temperature and pressure in the flask after combustion is complete.

Temperature (K): ________________	Pressure (atm): ________________

A similar combustion process occurs in gasoline engines to drive the engine's pistons. In the combustion reaction, gasoline vapor, which is mostly comprised of isooctane, combines with atmospheric oxygen to produce carbon dioxide and water:

$$2C_8H_{18(g)} + 25O_{2(g)} \rightarrow 16CO_{2(g)} + 18H_2O_{(g)}$$

e) The Ferrari 458 Italia has a fuel tank capacity of 86.0 L, and the density of isooctane is 0.703 g·mL^{-1}. Assuming gasoline is pure isooctane, calculate how many kilograms of CO_2 the 458 Italia releases into the environment per tank.

Mass of CO_2 (kg): ________________

f) The standard enthalpy change of octane combustion is $\Delta H°_{rxn} = -10{,}940$ kJ, and the average fuel economy of a Ferrari 458 Italia is 14 mpg. A round trip between Simon's home and his high school is 10 miles. If Simon were to commute to and from school by bike, he would burn about 298 kcal. How much energy would Simon save per school year (180 days) by biking to school instead of driving his Ferrari (1 L = 0.264 gal)?

Energy Saved (MJ): ________________

g) The $\Delta H°_f$ of $CO_{2(g)}$ is -393.5 kJ·mol^{-1}. Determine the enthalpy of formation per mole of isooctane.

$\Delta H°_f$ $C_8H_{18(g)}$ (kJ·mol^{-1}): ________________

a	b	c	d	e	f	g	h	Total	
4	2	6	6	6	6	2	4	36	9%

PROBLEM 4
9% of total

a) Sulfur dioxide is formed when sulfur is burned in the presence of oxygen. A small power plant produces 2.09 kg of sulfur dioxide per hour. Using the following information, calculate how much energy this power plant produces per hour through the formation of sulfur dioxide from sulfur:

$2S_{(s)} + 3O_{2(g)} \rightarrow SO_{3(g)}$ $\Delta H° = –791.6$ kJ

$2SO_{3(g)} \rightarrow 2SO_{2(g)} + O_{2(g)}$ $\Delta H° = 198.0$ kJ

Energy Produced (kJ): ________________

b) Sulfur dioxide is released into the atmosphere with oxygen and water vapor, which may combine and condense to form sulfuric acid (H_2SO_4). Find the chemical equation that represents this reaction

c) Recall that the enthalpy of formation for water vapor is –241.818 kJ·mol^{-1}. The standard entropy of formation for this reaction is $\Delta S°_{rxn} = –732$ J, and the standard enthalpy of formation for sulfuric acid is $\Delta H° = –814$ kJ·mol^{-1}. Determine $\Delta G°_{rxn}$ at 298 K under standard conditions.

$\Delta G°_{rxn}$ (kJ): ________________

d) A curious student wants to find the molar heat of neutralization between sulfuric acid and sodium hydroxide. She fills a calorimeter up with 50.0 mL of a 1.00 M NaOH solution, and neutralizes the base 6.00 M H_2SO_4. Both solutions start at temperatures of 18.0°C, and the calorimeter reaches a maximum temperature of 27.4°C during neutralization. Determine the molar heat of neutralization for this reaction. (Assume the density of water is 1.00 $g \cdot mL^{-1}$)

ΔH_{neut} ($kJ \cdot mol^{-1}$): ________________

e) In real calorimeters, most of the heat released by the bomb is absorbed by the water, but a certain amount is also absorbed by the metal and insulation surrounding the water tank. This loss may be accounted for by a calorimeter constant. To determine the calorimeter constant of her calorimeter, the student mixes 72.55 mL of water at 71.6°C into her calorimeter, which contained 58.85 mL of water at 22.4°C. After equilibration, the final temperature of the calorimeter was 47.3°C. Calculate the calorimeter constant of the student's calorimeter.

Calorimeter constant ($J \cdot °C^{-1}$): ________________

f) Recalculate the molar heat of neutralization between sulfuric acid and sodium hydroxide from part (d), but this time, account for the energy lost to the calorimeter using the calorimeter constant you determined in part (e).

ΔH_{neut} (kJ·mol^{-1}): ________________

g) The literature value for the molar heat of neutralization between sulfuric acid and sodium hydroxide is 55.8 kJ/mol. Using the experimental value from part (f), calculate the student's percent error.

Percent Error: ________________

h) After the experiment was complete, the student accidentally spilled 34.0 mL of the 6.0 M sulfuric acid onto the floor while cleaning up. She immediately neutralized the acid by pouring sodium hydrogen carbonate onto the spill:

$$H_2SO_{4(aq)} + 2NaHCO_{3(s)} \rightarrow Na_2SO_{4(aq)} + 2H_2O_{(l)} + 2CO_{2(g)}$$

Determine the volume of CO_2 released by this reaction at 25°C and 1 atm.

Volume CO_2 (L): ________________

a	b	c	d	e	f	g	h	i	j	Total	
4	4	2	6	4	4	3	6	2	3	38	12%

PROBLEM 5
12% of total

High concentrations of carbon dioxide in the atmosphere can prove fatal to humans. In the small confines of the Apollo Command/Service Modules (CSMs), the concentration of carbon dioxide builds up quickly through regular exhalation, and so the Apollo missions employed "Contaminate Control Cartridges" (CCCs), which contained the sorbent lithium hydroxide (LiOH), to remove exhaled carbon dioxide. The chemical reaction between lithium hydroxide and carbon dioxide is represented by the following equation:

$$2LiOH_{(s)} + CO_{2(g)} \rightarrow Li_2CO_{3(s)} + H_2O_{(g)}$$

a) Determine this reaction's standard enthalpy change (ΔH°_{rxn}) using the following information:

$LiOH_{(s)} + H_2O_{(g)} \rightarrow LiOH{\cdot}H_2O_{(s)}$ $\Delta H^\circ = -61.27$ kJ

$Li_2CO_{3(s)} + 3H_2O_{(g)} \rightarrow 2LiOH{\cdot}H_2O_{(s)} + CO_{2(g)}$ $\Delta H^\circ = -28.12$ kJ

ΔH°_{rxn} (kJ): ________________

b) Determine the standard entropy change for the removal of CO_2 using the following table:

Substance	**ΔS°_{rxn} J·mol^{-1}**
$LiOH_{(s)}$	42.8
$CO_{2(g)}$	213.7
$Li_2CO_{3(s)}$	90.2
$H_2O_{(g)}$	189.0

ΔS°_{rxn} (J): ________________

c) Is this reaction spontaneous under standard conditions at 298 K? Justify your answer.

Spontaneous	Non-spontaneous

Justification:

The liquid oxygen tanks aboard the CSMs of the Apollo missions were primarily responsible for electricity production via hydrogen fuel cells. 56 hours into the Apollo 13 lunar mission, the fans within the CSM's two oxygen tanks were turned on to "cryo-stir" the oxygen. The exposed fan wires of oxygen tank no. 2 shorted and ignited the pure oxygen environment. This fire rapidly increased the pressure inside the tank, causing the no. 2 oxygen tank to explode. Damaged by the adjacent explosion, the no. 1 tank gradually leaked oxygen until it was entirely depleted. All the oxygen stores of the CSM were lost within about 3 hours. Without power, the three-man crew of Apollo 13 had to abort the moon landing and relocate into the lunar module, which acted as their lifeboat for the next 95 hours of the mission (until reentry). Fortunately, the lunar module contained enough oxygen to sustain the crew for this duration; however, the carbon dioxide scrubber aboard the lunar module was designed only with enough LiOH to support two men for a 36-hour moon mission — not three men for a 95-hour trip back to earth.

d) The volume of the lunar module is 6.7 m^3, and each astronaut exhaled about 18.2 mol CO_2 per day. The pressure of the lunar module was kept at 1 atm, but because the astronauts could not afford the power necessary to heat the cabin, the temperature dropped as low as 4°C. If the fatal concentration of carbon dioxide is 100,000 ppm, how long would the astronauts have survived using the lunar module's CCC?

Hours: ________________

e) Miraculously, the Apollo 13 crew managed to MacGyver a scrubber from the powerless CSM, which was square-shaped, into the scrubber socket in the lunar module, which was circular-shaped. If the square scrubber from the CSM was designed to support three astronauts for 200 hours (about eight days), how much lithium hydroxide does it contain?

Mass (kg): ________________

The solid rocket boosters that are used to launch the Space Shuttle into orbit use a solid mixture of ammonium perchlorate (oxidizer), atomized aluminum powder (fuel), iron oxide (catalyst), PBAN (binder/fuel), and an epoxy curing agent. The primary reaction that occurs during liftoff is summed up by the following explosive chemical reaction:

$$3Al_{(s)} + 3NH_4ClO_{4(s)} \rightarrow Al_2O_{3(s)} + AlCl_{3(s)} + 6H_2O_{(g)} + 3NO_{(g)} + \text{heat}$$

f) The sudden appearance of hot gaseous products in a small initial volume leads to rapid increases in pressure and temperature, which give the rocket thrust. Calculate the total pressure of gas that would be produced at 3200°C by igniting 345,000 kg of ammonium perchlorate in a volume of 5730 m^3. (The molar mass of ammonium perchlorate is 117.49 $g\cdot mol^{-1}$)

Total Pressure (atm): ________________

g) This gas mixture then cools and expands until it reaches a temperature of 200°C and a pressure of 3.20 atm. Calculate the volume occupied by the gas mixture after this expansion has occurred.

Volume (m^3): ________________

h) Under extremely high pressures and temperatures, such as those within a solid rocket booster during lift-off, the behavior of a gas will deviate from the ideal gas law. In 1873, Johannes D. van der Waals proposed a modification to the ideal gas law that accounts for intermolecular forces under non-ideal conditions:

$$[P + a(n/V)^2](V/n - b) = RT$$

The van de Waals equation applies strictly to pure, real gases — not to mixtures; however, for a mixture such as the one that results from the reaction within a solid rocket booster, it may still be possible to define effective *a* and *b* parameters to relate total pressure, volume, temperature, and the total number of moles. Suppose the gas mixture has a = 12.00 atm·L^2·mol^{-2} and b = 0.0251 L·mol^{-1}. Recalculate the pressure of the gas mixture from part (f) using the van der Waals equation.

Total Pressure (atm): ________________

i) Why is this pressure higher/lower than the pressure calculated in part (f)?

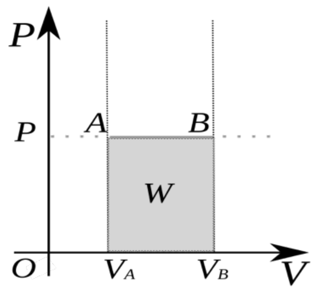
j) Nitric oxide (NO) readily combines with oxygen to form the harmful pollutant nitrogen dioxide (NO_2). Determine how much nitric oxide a space shuttle launch, which uses two solid rocket boosters, releases into the atmosphere.

Mass NO (kg): ________________

a	b	c	d	e	f	g	h	i	j	Total	
2	3	2	6	8	4	5	4	2	2	38	12%

PROBLEM 6
12% of total

a) Consider a diatomic gas that isobarically expands in a piston from V_A to V_B:



The work done by the gas as it moves from A to B is equivalent to the area under the curve. If V_B is twice the volume of V_A, determine how much work is done by the gas in terms of pressure *P* as it moves from A to B and B to A.

W_{by} A to B: ________________

W_{by} B to A: ________________

b) In fact, the work done by the gas as it moves between any two points on a PV graph is equivalent to the area under the path it takes. Determine the work done by a gas as it isochorically (constant volume) heats from P_0 to $2P_0$, and the work done by a gas as it isothermally expands from V_0 to $2V_0$ in terms of number of moles *n*, the gas constant *R*, and temperature *T*. (Hint: the area under the curve $y = 1/x$ from x_0 to x_f is $\ln(x_f/x_0)$)

W_{by} (isochoric): ________________

W_{by} (isothermal): ________________

c) For a diatomic adiabatic expansion (where $PV^{7/5}$ = constant), no heat is added to the gas, and the change in internal energy is the product of its heat capacity at constant volume C_v and its change in temperature ΔT. The heat capacity of a diatomic gas at constant volume is equivalent to $5/2 \cdot n \cdot R$. Determine the work done by a gas that heats (and expands) adiabatically from 50°C to 70°C in terms of n and R.

W_{by} (adiabatic): ________________

d) The change in internal energy for both isobaric and isochoric processes is the same as the change in internal energy for an adiabatic process. Determine the heat added to a gas isothermally compressed from $2P_0$ to P_0 in terms of n, R, and T, as well as the heat added to diatomic gases heated from 50°C to 70°C under isothermal and isobaric conditions in terms of n and R.

Q (isothermal): ________________

Q (isobaric): ________________

Q (isochoric): ________________

e) 1.00 moles of a diatomic gas at a temperature of 18.0°C adiabatically expands from 3.00 L to 5.95 L. Determine the final temperature and pressure of this gas, as well as the heat added and work done by the gas during this transformation. (Take Q_{in} to be positive)

T_f (K): ________________

P_f (atm): ________________

Q_{in} (J): ________________

W_{by} (J): ________________

f) This gas then isochorically decompresses such that its pressure halves. Calculate the final temperature and pressure of this gas, as well as the heat lost and the work done by the gas during this transformation. (Take Q_{out} to be positive)

T_f (K): ________________

P_f (atm): ________________

Q_{out} (J): ________________

W_{by} (J): ________________

g) Next, this gas isobarically warms to 18.0°C. Calculate the final volume of this gas, as well as the heat added and the work done by the gas. (Recall that 1 L·atm = 101.33 J)

V_f (L): ________________

Q_{in} (J): ________________

W_{by} (J): ________________

h) Finally, the gas isothermally returns to its initial volume of 3.00 L at 18°C. Determine the heat lost and the work done by the gas during this transformation.

Q_{out} (J): ________________

W_{by} (J): ________________

i) Determine the net work done by this four-part process.

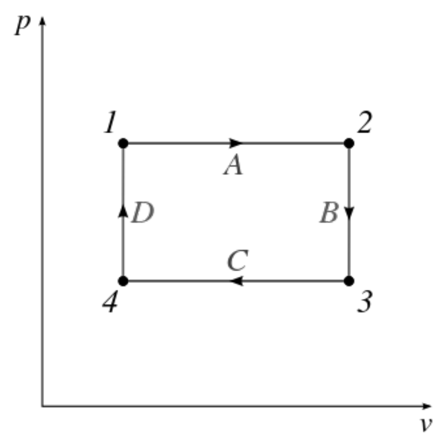
Net W_{by} (J): ________________

j) This gas has a density of 6.7×10^{-4} $g \cdot mL^{-1}$ at the initial (and final) conditions of this process. Determine the identity of this gas. Box your answer.

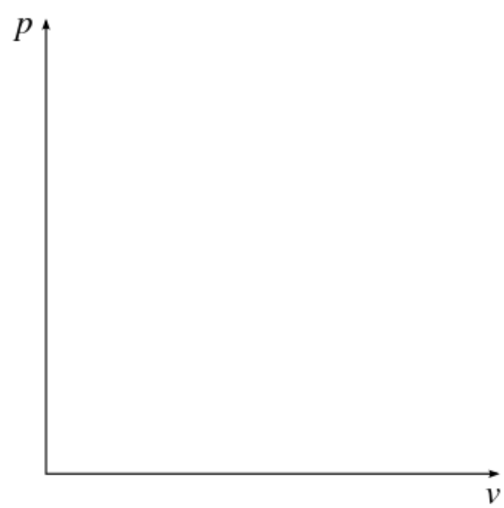
a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	Total	
8	4	2	2	6	2	3	5	5	5	2	4	4	2	6	60	15%

PROBLEM 7
15% of total

The thermodynamic transformations from problem 6 may combined in series to construct a closed "heat engine." As an example, the following diagram is a very simple heat engine that isobarically expands from 1 to 2, isochorically cools from 2 to 3, isobarically shrinks from 3 to 4, and isochorically heats from 4 back to 1. The net work done by the cycle is the area enclosed by the PV curves.



a) In cars, gasoline engines employ the four-stroke Otto cycle to drive pistons. First, fuel is drawn into the cylinder as the piston isobarically expands from V_1 to V_2. At this point (point A), the piston adiabatically compresses the gas back to V_1 (point B). Next, a spark ignites the fuel, isochorically heating it to point C. Then, the piston adiabatically expands to V_2 (point D), after which the gas isochorically cools down and returns to point A. Finally, the exhaust valve opens and the gaseous mixture in the cylinder is vented out of the car as the piston returns to V_1. Sketch this cycle on a PV diagram starting and ending at point A (you may ignore the fuel intake and exhaust strokes). Indicate direction with arrows and label points A–D as well as V_1 & V_2.



b) Circle <u>all statements</u> that are true for each process in the Otto cycle:

$A \rightarrow B$

$Q = 0$	$Q_{in} > 0$	$Q_{out} > 0$	$W_{by} = 0$	$W_{by} > 0$	$W_{by} < 0$

$B \rightarrow C$

$Q = 0$	$Q_{in} > 0$	$Q_{out} > 0$	$W_{by} = 0$	$W_{by} > 0$	$W_{by} < 0$

$C \rightarrow D$

$Q = 0$	$Q_{in} > 0$	$Q_{out} > 0$	$W_{by} = 0$	$W_{by} > 0$	$W_{by} < 0$

$D \rightarrow A$

$Q = 0$	$Q_{in} > 0$	$Q_{out} > 0$	$W_{by} = 0$	$W_{by} > 0$	$W_{by} < 0$

c) Determine Q_{in} and Q_{out} for the Otto cycle in terms of C_v, and temperatures T_A, T_B, T_C, and T_D. (Remember that Q_{out} should be a positive value).

Q_{in}: ________________

Q_{out}: ________________

d) The efficiency of a heat engine is given by $\eta = W_{netl}/Q_{in}$. Recall that $W = Q_{in} - Q_{out}$. Rewrite the equation for the efficiency of the Otto cycle in terms of temperatures T_A, T_B, T_C, and T_D.

$\eta =$ ________________

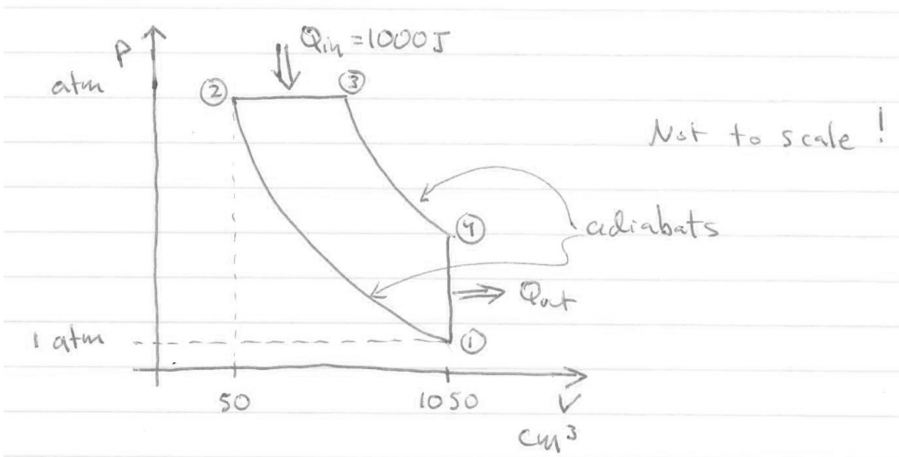
e) Assume that gasoline mixture is a diatomic gas. Recall that for a diatomic, adiabatic process, $PV^{7/5}$ = constant. Now solve for the efficiency of the Otto cycle in terms of *r*, where *r* is the compression ratio V_2/V_1. (Hint: multiply out T_A/T_B from one of the terms in your answer to (d))

η = ________________

f) A typical compression ratio for a car is 10:1. Use your answer from part (e) to calculate the ideal efficiency of a gasoline engine. (The actual efficiency is about 15 – 20%)

η (gasonline engine) : ________________

A diesel engine differs from a gasoline engine in that the isochoric spark plug process (B → C) is substituted for an explosive isobaric process. This explosion is achieved through rapid adiabatic compression of the diesel fuel over a much greater compression ratio (hence the larger engine). Consider the following diagram.



g) The temperature at point 1 is 25°C. Determine *P, V,* and *T* at point 1.

P_1 (atm): ________________

V_1 (L): ________________

T_1 (K): ________________

h) Determine *P, V,* and *T* at point 2.

P_2 (atm): ________________

V_2 (L): ________________

T_2 (K): ________________

i) Determine *P, V,* and *T* at point 3.

P_3 (atm): ________________

V_3 (L): ________________

T_3 (K): ________________

j) Determine *P, V,* and *T* at point 4.

P_4 (atm): ________________

V_4 (L): ________________

T_4 (K): ________________

k) Calculate the work done by the engine during the isobaric leg of this cycle.

W_{by} (J): _________________

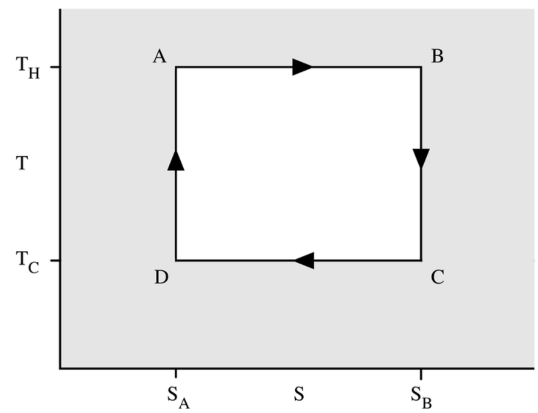
l) Calculate the efficiency of this diesel engine.

η (diesel engine) : _________________

m) This engine operates at 2400 RMO and has 4 cylinders each going through the cycle shown. Calculate the horsepower of this engine. (1 hp = 745.7 W)

Horsepower (hp) : _________________

The Carnot cycle is the most efficient cycle to operate between two temperatures. Consider the Carnot cycle as represented by a temperature vs. entropy graph:



n) Identify the transformation occurring during each leg of the processes.

A → B

Isothermal	Isochoric	Isobaric	Adiabatic

B → C

Isothermal	Isochoric	Isobaric	Adiabatic

C → D

Isothermal	Isochoric	Isobaric	Adiabatic

D → A

Isothermal	Isochoric	Isobaric	Adiabatic

o) The area enclosed by the TΔS curves is equivalent to $W = Q_{in} - Q_{out}$. Explain why the Carnot cycle is the most efficient cycle to operate between any two temperatures.