

General Directions for Grader

- Award partial credit for work shown **at your own discretion**. The partial credit statements in the key are merely just **suggestions**. However you end up grading, make sure to **be consistent**.
- Answers should generally not receive more partial credit than 2 points less than total points for a question (because units).
- Correct answers without units (or with improper units) **will not receive full credit**.
- 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.
- Please double check your grading. Triple check the top few scorers.
- Completely illegible answers do not receive full credit, but please try to decode the student's scribbles if possible.
- Some errors should carry through. You will need a calculator to check students' work
- Award full credit for answers within ± 1 of last sig fig (NB there are likely sig fig and rounding errors in the key)

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

PERIODIC TABLE OF THE ELEMENTS

1 1A																	18 8A	
1 H 1.008	2 2A												13 3A	14 4A	15 5A	16 6A	17 7A	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	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	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)					

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)	$[\text{KNO}_3]$ (M)	a) Crystal Temperature ($^{\circ}\text{C}$)
1			8 points: <ul style="list-style-type: none"> • 1(x6) for each box filled in with a temperature between 20°C and 100°C • 2 points if temperatures decrease
2			
3			
4			
5			
6			

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

2 points:

- 2 points for correct answer
- Partial credit awarded for work shown properly relating K to ionic concentrations



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 ($\text{kJ} \cdot \text{mol}^{-1}$)
1				
2				
3				
4				
5				
6				

2 points:

- 1 point for decreasing K_{sp}
- 1 point bound from 100 to 10

6 points:

- 4 points for increasing ΔG
- 2 points bound from -15 to -5

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 $(-\Delta H^\circ/R)$. Box your answer.

2 points:

- 1 point mathematically equivalent statement to answer
- 1 point $y = mx + b$ form (R can be moved to other side of equation and negatives can be flipped)

$$\ln k = -H/R \cdot (1/T) + S/R$$

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

<p>6 points:</p> <ul style="list-style-type: none"> • 2(x3) points for a proper calculation between a unique pair of points 	
<p>5 points:</p> <ul style="list-style-type: none"> • 5 points for accepted value <u>near</u> answer • answers more than 5 kJ off receive 4 points max (and so on) • -1 point for answer without or improper units (must be kJ or J per mole) <p>Accepted $\Delta H = 34.89 \text{ kJ} \cdot \text{mol}^{-1}$</p>	<p>5 points:</p> <ul style="list-style-type: none"> • 5 points for accepted value <u>near</u> answer • answers more than 15 J off receive 4 points max (and so on) • -1 point for answer without or improper units (must be kJ or J per mole) <p>Accepted $\Delta S = 115.6 \text{ J} \cdot \text{mol}^{-1}$</p>

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

1 point if above leads to $\Delta G > 0$: Endergonic	½ point if above answer leads to $\Delta G < 0$
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Is ΔH endothermic or exothermic?

1 point if accepted $\Delta H > 0$: Endothermic	½ point if accepted $\Delta H < 0$
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Is ΔS negative or positive?

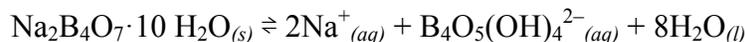
½ point if accepted $\Delta S < 0$	1 point if accepted $\Delta S > 0$: Positive
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Why is this so (referring to ΔS relative to 0)?

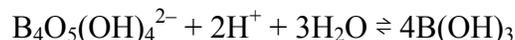
<p>2 points:</p> <ul style="list-style-type: none"> • Answer mentions that dissolution increases entropy
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Part II – Related Application

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



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



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

3 points:

- 3 points for correct answer
- 1 point partial credit for answers in terms of Borate w/ a factor of 4 or exponent of 3
- 1 point partial credit for work showing dissolution equilibrium and/or stoichiometry approach

$$K_{sp} = 4[\text{B}_4\text{O}_5(\text{OH})_4^{2-}]^3$$

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 .

8 points:

- 8 points for correct answer
 - 7 points without correct units (kJ or J per mole)
- 2 points partial credit awarded for showing some form of $-RT\ln K = \Delta G$
- 3 points partial credit awarded for proper dimensional analysis (even if calculation is wrong)

$$\Delta G = -10.9 \text{ kJ} \cdot \text{mol}^{-1}$$

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

3 points:

- 3 points for correct answer

Percent Error: 2.85%

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

3 points:

- 1 point for negative and constant slope
- 1 point for x axis labeled $1/T$
- 1 point for y axis labeled $\ln(4([\text{Borate}])^3)$

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?

2 points: Smaller	Same	Larger
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b) Which of the following gases is responsible for the depletion of the ozone layer?

CH ₃ F	CO ₂	2 points: CCl ₃ F	CF ₄	NO ₂
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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 ΔH is the heat of vaporization for the liquid?

$P^\circ \cdot V = n \cdot R \cdot T$	$A \cdot P^\circ = \Delta H \cdot V / (R \cdot T) + C$	$\ln(P^\circ) = A \cdot \Delta H / (R \cdot T)$	2 points: $\ln(P^\circ) = C - \frac{\Delta H}{(R \cdot T)}$
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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 ($P \cdot V^{7/5} = \text{constant}$). The initial pressure is 1.54 atm, and the initial temperature is 25.00°C. Calculate the final temperature of the gas.

<p>4 points:</p> <ul style="list-style-type: none"> 4 points for correct answer <ul style="list-style-type: none"> 3 points without correct units (K) 1 point partial credit awarded for showing and applying $PV^{7/5}$ 1 point partial credit awarded for taking the above and solving for $TV^{2/5}$ <p>Temperature (K): 393.21 K</p>

e) What is the average molecular velocity of O₂ gas at STP?

3 points:

- 3 points for correct answer
 - 2 points without correct units (m/s)
- 1 point partial credit for showing proper calculation

Velocity (m/s): 461.423 m/s

f) Label the following statements true or false. **1(x5) point** for each correct answer:

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?

3 points: Isothermal	Isochoric	Isobaric	Adiabatic	Such a process would violate the 2 nd law of thermodynamics
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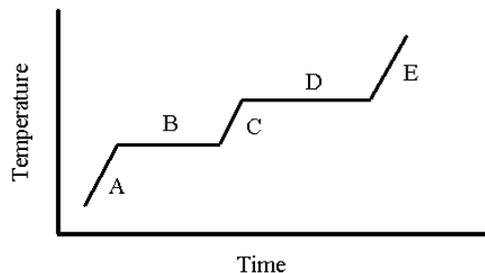
h) Use the phase diagram (for some arbitrary substance) on the right to answer the next two questions. **2 points**

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

A	1 point: B	C	D	E
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If heat was added at a constant rate for this diagram, could this substance have been water?

Yes	1 point: No
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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.

9 points: <ul style="list-style-type: none"> • 4(x2) for correct answer of H₂ or O₂ <ul style="list-style-type: none"> ○ award only 3 points if missing correct units (any valid measure of pressure) • 1 point for correct total pressure <ul style="list-style-type: none"> ○ ½ point if missing correct units (pressure) • 1 point partial (x3) work support supporting each answer 		
$P_{\text{H}_2} = 19.4 \text{ atm}$	$P_{\text{O}_2} = 7.77 \text{ atm}$	$P_{\text{total}} = 27.2 \text{ atm}$

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.

4 points: <ul style="list-style-type: none"> • 1 point for <u>all</u> correct states • 2 points for balanced equation (i.e. correct coefficients) • 1 point for <u>all</u> correct products/reactants $2\text{H}_2 (\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2\text{H}_2\text{O} (\text{g})$

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

6 points: <ul style="list-style-type: none"> • 2(x3) awarded for each correct answer <ul style="list-style-type: none"> ○ award only 1 point if missing correct units (mol) • partial credit awarded if consistent with the student's answer to (b) & has supporting calculations 		
$\text{H}_2 (\text{mol}) = 2 \text{ mol}$	$\text{H}_2 (\text{mol}) = 0 \text{ mol}$	$\text{H}_2\text{O} (\text{mol}) = 8 \text{ mol}$

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

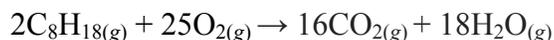
10 points:

- 5(x2) points for each correct answer
 - award only 4 points if missing correct units
- 1 point PC for finding old temp
- 1 point PC for applying $PV=nRT$
- 1 point PC for combined heat capacities

Temperature (K): 3535 K

Pressure (atm): 145.0 L

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:



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

4 points:

- 4 points for correct answer
 - 3 max without proper units (MJ)
- 1 PC for appropriate supporting calculation

Mass of CO_2 (kg): 186.34 kg

f) The standard enthalpy change of octane combustion is $\Delta H^\circ_{rxn} = -10,940 \text{ kJ}$, 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)?

8 points:

- 8 points for correct answer
 - 7 max without proper units (MJ)
- PC for supporting calculations

Energy Saved (MJ): 32560 MJ

g) The ΔH°_f of $\text{CO}_{2(g)}$ is $-393.5 \text{ kJ}\cdot\text{mol}^{-1}$. Determine the enthalpy of formation per mole of isooctane.

4 points:

- 4 points for correct answer
 - 3 max without proper units
- PC for supporting calculations

$\Delta H^\circ_f \text{ C}_8\text{H}_{18(g)}$ ($\text{kJ}\cdot\text{mol}^{-1}$): $-145.9 \text{ kJ}\cdot\text{mol}^{-1}$

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:



4 points

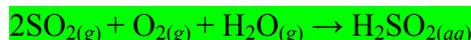
- 4 points for correct answer
 - 3 max without proper units
- 1 point PC for application of Hess' law
- 1 point PC for dimensional analysis

Energy Produced (kJ): -9680 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

2 points:

- 1 point for correct balanced equation and correct product/reactants
- 1 point for correct states



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

6 points:

- 6 points for correct answer
 - 5 max without proper units
- PC for proper supporting calculations

ΔG°_{rxn} (kJ): 240 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 H₂SO₄. 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·mL⁻¹)

6 points:

- 6 points for correct answer
 - 5 max without proper units
- PC for proper supporting calculations

ΔH_{neut} (kJ·mol⁻¹): -42.6 kJ·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.

6 points:

- 6 points for correct answer
 - 5 max without proper units
- PC for proper supporting calculations

Calorimeter constant (J·°C⁻¹): 62.6 J·°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).

6 points:

- 6 points for correct answer
 - 5 max without proper units
- PC for proper supporting calculations

ΔH_{neut} (kJ·mol⁻¹): 54.4 kJ·mol⁻¹

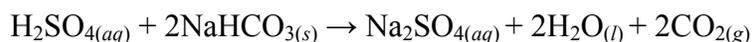
g) The literature value for the molar heat of neutralization between sulfuric acid and sodium hydroxide is 55.8 kJ/mol. Using the experimental value from part (f), calculate the student's percent error.

2 points:

- 2 points for correct answer
- 1 point PC for correct application of percent error but using values from above answers that themselves are incorrect

Percent Error: 2.5%

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:



Determine the volume of CO₂ released by this reaction at 25°C and 1 atm.

4 points:

- 4 points for correct answer
 - 3 max without proper units
- Up to 2 points PC for supporting calculations (like dimensional analysis)

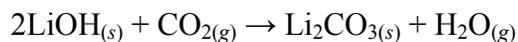
Volume CO₂ (L): 9.98 L

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

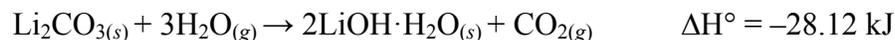
PROBLEM 5

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:



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



4 points:

- 4 points for correct answer
 - 3 max without proper units
- PC for correct application of Hess’ law and other calculations

ΔH°_{rxn} (kJ): -94.42 kJ

b) Determine the standard entropy change for the removal of CO₂ using the following table:

Substance	$\Delta S^\circ_{rxn} \text{ J}\cdot\text{mol}^{-1}$
LiOH _(s)	42.8
CO _{2(g)}	213.7
Li ₂ CO _{3(s)}	90.2
H ₂ O _(g)	189.0

4 points:

- 4 points for correct answer
 - 3 max without proper units
- PC for supporting calculations

ΔS°_{rxn} (J): -20.1 J

c) Is this reaction spontaneous under standard conditions at 298 K? Justify your answer. **2 points**

Spontaneous	1 point: Non-spontaneous
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1 point:

- 1 point awarded if the student's answer correctly justifies the above by comparing ΔG to 0. For instance, a point will still be awarded if the student incorrectly circled spontaneous but properly justified it with $\Delta G < 0$

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?

6 points:

- 6 points for correct answer
 - 5 max without proper units (hrs)
- PC awarded for supporting calculations

Hours: 37 hours

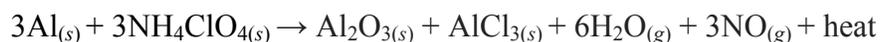
e) Miraculously, the Apollo 13 crew managed to MacGyver a scrubber from the powerless CSM, which was square-shaped, into the scrubber socket in the lunar module, which was circular-shaped. If the square scrubber from the CSM was designed to support three astronauts for 200 hours (about eight days), how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

4 points:

- 4 points for correct answer
 - 3 max without proper units (kg)
- PC awarded for supporting calculations

Mass (kg): 21.8 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:



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 m³. (The molar mass of ammonium perchlorate is 117.49 g·mol⁻¹)

4 points:

- 4 points for correct answer
 - 3 max without proper units (atm)
- PC awarded for supporting calculations

Total Pressure (atm): 438 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.

3 points:

- 3 points for correct answer
 - 2 max without proper units (m³)
- PC awarded for supporting calculation

Volume (m³): 107,000 m³

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 $a = 12.00 \text{ atm}\cdot\text{L}^2\cdot\text{mol}^{-2}$ and $b = 0.0251 \text{ L}\cdot\text{mol}^{-1}$. Recalculate the pressure of the gas mixture from part (f) using the van der Waals equation.

6 points:

- 6 points for correct answer
 - 5 max without proper units (atm)
- PC awarded for supporting calculations

Total Pressure (atm): 427 atm

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

2 points:

- 1 point for answer that primarily justifies this phenomenon by stating that water has high IMF and therefore decreases pressure
- 1 point for mentioning the above and stating that water is most of the product

j) Nitric oxide (NO) readily combines with oxygen to form the harmful pollutant nitrogen dioxide (NO₂). Determine how much nitric oxide a space shuttle launch, which uses two solid rocket boosters, releases into the atmosphere.

3 points:

- 3 points for correct answer
 - 2 max without proper units (kg)
- PC awarded for supporting calculation

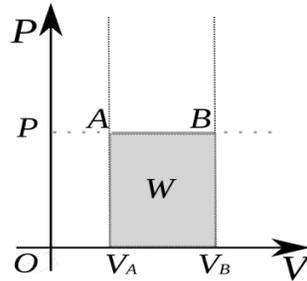
Mass NO (kg): 176,000 kg

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.

2 points total

1 point: $W_{\text{by A to B}}: 2P$

1 point: $W_{\text{by B to A}}: -2P$

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 $\ln(x_f/x_0)$)

3 points total

1 point: $W_{\text{by (isochoric)}}: 0$

2 points: $W_{\text{by (isothermal)}}: nRT\ln(2)$

c) For a diatomic adiabatic expansion (where $PV^{7/5} = \text{constant}$), 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 .

2 points total (1 point PC for calculation with correct approach)

2 points: W_{by} (adiabatic): $-50nR$

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 .

6 points total (1 point PC each for calculations with correct approach)

2 points: Q (isothermal): $nRT\ln(2)$

2 points: Q (isobaric): $70nR$

2 points: Q (isochoric): $50nR$

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)

8 points total (up to 4 points PC for calculations with correct approach)

- **-1/2 point(x4) for each correct answer missing correct units**

2 points: T_f (K): 221 K

2 points: P_f (atm): 3.05 atm

2 points: Q_{in} (J): 0 J

2 points: W_{by} (J): 1450 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)

4 points total (up to 2 points PC for calculations with correct approach)

- -1/2 point(x4) for each correct answer missing correct units

1 point: T_f (K): 111K

1 point: P_f (atm): 1.53 atm

1 point: Q_{out} (J): 2300 J

1 point: W_{by} (J): 0 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 $1 \text{ L}\cdot\text{atm} = 101.33 \text{ J}$)

5 points total (up to 3 points PC for calculations with correct approach)

- -1/2 point(x3) for each correct answer missing correct units

1 point: V_f (L): 15.6 L

2 points: Q_{in} (J): 5250 J

2 points: W_{by} (J): 1500 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.

4 points total (up to 2 points PC for calculations with correct approach)

- -1/2 point(x2) for each correct answer missing correct units

2 points: Q_{out} (J): 3400 J

2 points: W_{by} (J): -3400 J

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

2 points:

- 2 points awarded for correct answer
 - 1.5 points max without correct units
- 1 point PC for supporting calculation

Net W_{by} (J): -450 J

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

2 points:

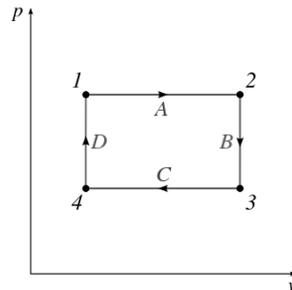
- 2 points awarded for correct answer
- 1 point PC for supporting calculation

H_2

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

PROBLEM 7
15% of total

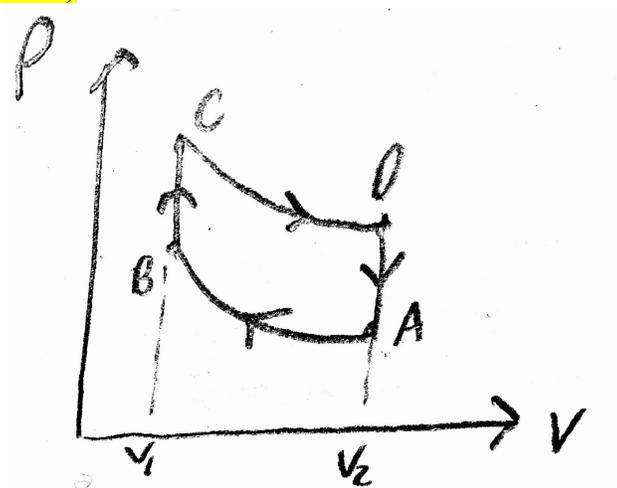
The thermodynamic transformations from problem 6 may be combined in series to construct a closed “heat engine.” As an example, the following diagram is a very simple heat engine that isobarically expands from 1 to 2, isochorically cools from 2 to 3, isobarically shrinks from 3 to 4, and isochorically 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.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 .

8 points:

- 1/2 (x4) points awarded each labeled point (A through D)
- 1 point (x2) each for V_1 , V_2
- 1 point (x4) for each curve drawn with correct shape AND proper direction — see below diagram (more or less)



b) Circle all statements that are true for each process in the Otto cycle: **4 points**

A → B

½ point: $Q = 0$	$Q_{in} > 0$	$Q_{out} > 0$	$W_{by} = 0$	$W_{by} > 0$	½ point: $W_{by} < 0$
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B → C

$Q = 0$	½ point: $Q_{in} > 0$	$Q_{out} > 0$	½ point: $W_{by} = 0$	$W_{by} > 0$	$W_{by} < 0$
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C → D

½ point: $Q = 0$	$Q_{in} > 0$	$Q_{out} > 0$	$W_{by} = 0$	½ point: $W_{by} > 0$	$W_{by} < 0$
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D → A

$Q = 0$	$Q_{in} > 0$	½ point: $Q_{out} > 0$	½ point: $W_{by} = 0$	$W_{by} > 0$	$W_{by} < 0$
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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).

2 points:
1 point: $Q_{in}: C_v(T_C - T_B)$
1 point: $Q_{out}: C_v(T_D - T_A)$

d) The efficiency of a heat engine is given by $\eta = W_{net}/Q_{in}$. 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 .

2 points:
2 points: $\eta = 1 - (T_D - T_A)/(T_C - T_B)$

e) Assume that gasoline mixture is a diatomic gas. Recall that for a diatomic, adiabatic process, $PV^{7/5} = \text{constant}$. 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))

6 points total (PC awarded for calculations with correct approach)

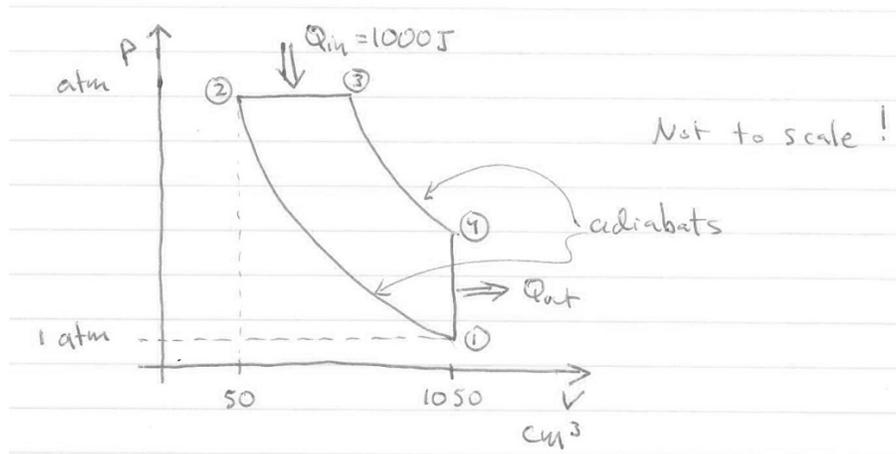
6 points: $\eta = 1 - (1/r)^{2/5}$

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%)

2 points:

2 points: η (gasoline engine): 60.2%

A diesel engine differs from a gasoline engine in that the isochoric spark plug process ($B \rightarrow C$) 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.

3 points:

- 1/2 point(x3) for each correct answer missing correct units

1 point: P_1 (atm): 1 atm

1 point: V_1 (L): 1.05 L

1 point: T_1 (K): 298 K

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

5 points:

- 1/2 point(x3) for each correct answer missing correct units

2 points: P_2 (atm): 71.0 atm

1 point: V_2 (L): .05 L

2 points: T_2 (K): 1007 K

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

5 points:

- -1/2 point(x3) for each correct answer missing correct units

1 point: P_3 (atm): 71.0 atm (same as last — consider PC)

2 points: V_3 (L): .09 L

2 points: T_3 (K): 1807 K

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

5 points:

- -1/2 point(x3) for each correct answer missing correct units

2 points: P_4 (atm): 2.27 atm

1 point: V_4 (L): 1.05 L

2 points: T_4 (K): 679 K

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

2 points:

2 points: W_{by} (J): 286 J

l) Calculate the efficiency of this diesel engine.

4 points:

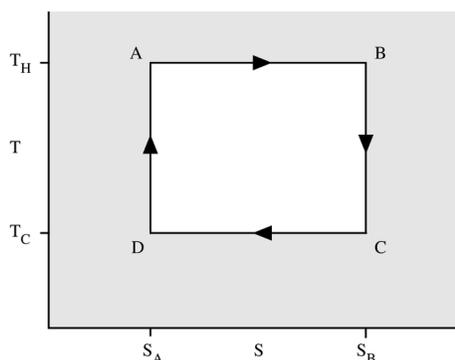
4 points: η (diesel engine): 66%

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)

4 points:

4 points: Horsepower (hp): 143 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. **2 points:**

A → B

½ point: Isothermal	Isochoric	Isobaric	Adiabatic
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B → C

Isothermal	Isochoric	Isobaric	½ point: Adiabatic
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C → D

½ point: Isothermal	Isochoric	Isobaric	Adiabatic
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D → A

Isothermal	Isochoric	Isobaric	½ point: Adiabatic
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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.

6points:

Correct answers should mention that for a cycle operating between two temperatures, the efficiency is the ratio between the white area in the above graph (work), and the white area + the grey area directly below the maximum and minimum entropy values (Q_{in}). The goal is to maximize W while minimizing the Q_{in} that does not contribute to W (the grey area). First, minimizing the Q_{in} that doesn't contribute to work is achieved by keeping the grey part of Q_{in} entire below the lower temperature. This results in the vertical adiabatic curves (i.e. the heat cycle operates between two entropy states). With this constraint established, maximizing W is achieved simply by filling the whole area of the rectangle (with edges S_A , S_B , T_H , T_C).