



NATIONAL MATH + SCIENCE INITIATIVE

AP CHEMISTRY

Thermodynamics

2016 EDITION
PRESENTER

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
140.12	140.91	144.24	(145)	150.4	151.97	157.25	158.93	162.50	164.93	167.26	168.93	173.04	174.97
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
232.04	231.04	238.03	237.05	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(260)

†Actinide Series:

2016 AP Chemistry - Thermodynamics: Enthalpy, Entropy, and Free Energy

AP Chemistry Equations & Constants

Throughout the test the following symbols have the definitions specified unless otherwise noted.

L, mL = liter(s), milliliter(s)

g = gram(s)

nm = nanometer(s)

atm = atmosphere(s)

mm Hg = millimeters of mercury

J, kJ = joule(s), kilojoule(s)

V = volt(s)

mol = mole(s)

ATOMIC STRUCTURE

$$E = h\nu$$

$$c = \lambda\nu$$

E = energy

ν = frequency

λ = wavelength

Planck's constant, $h = 6.626 \times 10^{-34}$ J s

Speed of light, $c = 2.998 \times 10^8$ m s⁻¹

Avogadro's number = 6.022×10^{23} mol⁻¹

Electron charge, $e = -1.602 \times 10^{-19}$ coulomb

EQUILIBRIUM

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}, \text{ where } a A + b B \rightleftharpoons c C + d D$$

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

$$= K_a \times K_b$$

$$\text{pH} = -\log [H^+], \text{ pOH} = -\log [OH^-]$$

$$14 = \text{pH} + \text{pOH}$$

$$\text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]}$$

$$\text{p}K_a = -\log K_a, \text{ p}K_b = -\log K_b$$

Equilibrium Constants

K_c (molar concentrations)

K_p (gas pressures)

K_a (weak acid)

K_b (weak base)

K_w (water)

KINETICS

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$t_{1/2} = \frac{0.693}{k}$$

k = rate constant

t = time

$t_{1/2}$ = half-life

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$P_A = P_{\text{total}} \times X_A, \text{ where } X_A = \frac{\text{moles A}}{\text{total moles}}$$

$$P_{\text{total}} = P_A + P_B + P_C + \dots$$

$$n = \frac{m}{M}$$

$$K = ^\circ\text{C} + 273$$

$$D = \frac{m}{V}$$

$$KE \text{ per molecule} = \frac{1}{2}mv^2$$

Molarity, M = moles of solute per liter of solution

$$A = abc$$

P = pressure

V = volume

T = temperature

n = number of moles

m = mass

M = molar mass

D = density

KE = kinetic energy

v = velocity

A = absorbance

a = molar absorptivity

b = path length

c = concentration

Gas constant, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$= 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$

$= 62.36 \text{ L torr mol}^{-1} \text{ K}^{-1}$

$1 \text{ atm} = 760 \text{ mm Hg}$

$= 760 \text{ torr}$

STP = 0.00°C and 1.000 atm

THERMOCHEMISTRY/ ELECTROCHEMISTRY

$$q = mc\Delta T$$

$$\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -RT \ln K$$

$$= -nFE^\circ$$

$$I = \frac{q}{t}$$

q = heat

m = mass

c = specific heat capacity

T = temperature

S° = standard entropy

H° = standard enthalpy

G° = standard free energy

n = number of moles

E° = standard reduction potential

I = current (amperes)

q = charge (coulombs)

t = time (seconds)

Faraday's constant, $F = 96,485 \text{ coulombs per mole of electrons}$

$$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$$



What I Absolutely Have to Know to Survive the AP Exam

The following might indicate the question deals with thermochemistry and thermodynamics:
calorimeter; enthalpy (ΔH); specific heat (C_p); endothermic; exothermic; heat (q); heat capacity (C); heat transfer; bond energy; entropy (ΔS); Gibb's free energy (ΔG); spontaneous; state function

Laws of Thermodynamics

Zeroth Law:	Heat flows from hot to cold
First Law:	Energy and matter are conserved
Second Law:	Matter tends towards chaos
Third Law:	Entropy of a pure crystal at 0K is zero

Thermodynamic Terms

What does each term tell us?

Enthalpy (ΔH)	Energy content	+ endothermic	– exothermic
Entropy (ΔS)	Disorder	+ increase in the dispersal of matter	– decrease in the dispersal of matter
Free energy (ΔG)	Thermodynamically favored or not favored	+ not thermodynamically favored	– thermodynamically favored
Equilibrium (K)	Extent of reaction	>1 reaction favors products	<1 reaction favors reactants

Internal Energy (ΔE) and Heat Flow

- Refers to all of the energy contained within a chemical system.
- Heat flow between the system and its surroundings involves changes in the internal energy of the system. It will either increase or decrease
 - Increases in internal energy may result in a
 - temperature increase
 - chemical reaction starting
 - phase change
 - Decreases in internal energy may result in a
 - a decrease in temperature
 - phase change
 - Note: even though the change in internal energy can assume several different forms, the amount of energy exchanged between the system and the surroundings can be accounted for **ONLY** by heat (q) and work (w)
 - $\Delta E = q + w$
 - Work (w) refers to a force acting on an object; in chemical processes this acting force is done **by** a gas through expansion or **to** a gas by compression.
 - This is referred to as “pressure/volume” work
 - Thus, $w = -P\Delta V$
 - Where P is constant external pressure (atm) and ΔV (L) is the change in volume of the system



Calculating Heat (q)

- Heat (q) gained or lost by a specific amount of a known substance can be calculated using the heat capacity of the substance and the change in temperature the system undergoes.
- Calorimetry
 - The process of experimentally measuring heat by determining the temperature change when a body absorbs or releases energy as heat.
- Coffee-cup calorimetry –use a Styrofoam cup, mix reactants that begin at the same temperature and look for change in temperature; the heat transfer is calculated from the change in temp.

$$q = mC\Delta T$$

- q = quantity of heat (Joules)
- ΔT is the change in temperature
 - $\Delta T = T_f - T_i$ (final – initial)
 - watch the sign; if the system loses heat to the surroundings then the $\Delta T = -$
- C_p = specific heat capacity ($J/g^\circ C$)
- m = mass in grams
- the specific heat of water (liquid) = $4.184 J/g^\circ C$

Also note:

- $q = -\Delta H$ at constant pressure

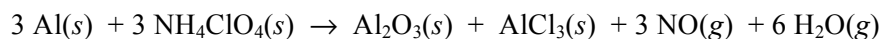
Enthalpy (ΔH)

Enthalpy
Heat content; ΔH
Endothermic (+) or Exothermic (–)
Calculating Enthalpy 5 Ways
Calorimetry (see above)
Enthalpy of formation, ΔH_f° (using table of standard values)
Hess's Law
Stoichiometry
Bond Energies

ΔH_f° – Enthalpy of Formation

- Production of **ONE MOLE** of compound FROM ITS ELEMENTS in their standard states ($^\circ$)
- Zero (0) for ELEMENTS in standard states: $25^\circ C$ (298 K), 1 atm, 1M

Big Mamma Equation: $\Delta H^\circ_{\text{rxn}} = \Sigma \Delta H^\circ_{\text{f (products)}} - \Sigma \Delta H^\circ_{\text{f (reactants)}}$

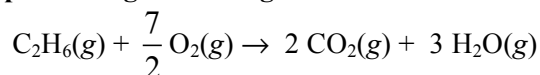


Substance	ΔH_f° (kJ/mol)
$\text{NH}_4\text{ClO}_4(s)$	–295
$\text{Al}_2\text{O}_3(s)$	–1676
$\text{AlCl}_3(s)$	–704
$\text{NO}(g)$	90.0
$\text{H}_2\text{O}(g)$	–242



Hess's Law

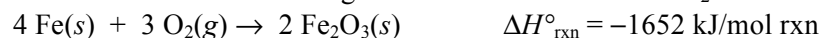
- Enthalpy is not dependent on the reaction pathway. If you can find a combination of chemical equations that add up to the desired *overall* equation, you can sum up the ΔH_{rxn} 's for the individual reactions to get the overall ΔH_{rxn} .
- Remember this:
 - First decide how to rearrange equations so reactants and products are on appropriate sides of the arrows.
 - If equations had to be reversed, change the sign of ΔH
 - If equations had to be multiplied to get a correct coefficient, multiply the ΔH by the coefficient
 - Check to ensure that everything cancels out to give you the correct equation.
 - Hint** It is often helpful to begin working backwards from the answer that you want!**



Using Stoichiometry to Calculate ΔH

- Often questions are asked about the enthalpy change for specific quantities in a reaction
- Use a little stoichiometry to solve these; just remember the $\Delta H^\circ_{\text{rxn}}$ is per mole and convert to the unit and quantity given

How much heat is released when 1.00 g iron is reacted with excess O_2 ?



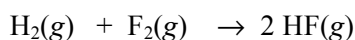
$$\text{heat released} = \frac{-1652 \text{ kJ}}{4 \text{ mol Fe}} \times \frac{1.00 \text{ g}}{55.85 \frac{\text{g}}{\text{mol}}} = -7.39 \text{ kJ per gram of Fe}$$

- the (–) represents the LOSS or release of heat
- can also write 7.39 kJ released per gram of Fe

Using Bond Energy to Calculate ΔH

- Be able to use individual Bond Energy data to calculate the overall enthalpy change for a reaction

$$\Delta H^\circ_{\text{rxn}} = \text{Sum of Bonds Broken} - \text{Sum of Bonds Formed}$$



Bond Type	Bond Energy
H–H	432 kJ/mol
F–F	154 kJ/mol
H–F	565 kJ/mol



Entropy (ΔS)

Entropy

- Dispersal of matter
- Less dispersal (–) or More dispersal (+)
- Calculating Entropy
 - Table of standard values
 - Hess's Law

- Entropy increases when:
 - Gases are formed from solids or liquids (most important!!!!)
 - $\text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{O}(\text{g})$
 - $\text{C}(\text{s}) + \text{CO}_2(\text{g}) \rightleftharpoons 2 \text{CO}(\text{g})$
 - A solution is formed
 - Volume is increased in a gaseous system (energy is more efficiently dispersed)
 - More complex molecules are formed

Big Mamma Equation II: $\Delta S^\circ_{\text{rxn}} = \Sigma \Delta S^\circ_{\text{(products)}} - \Sigma \Delta S^\circ_{\text{(reactants)}}$
 $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{SO}_3(\text{g})$

Substance	$S^\circ (\text{J K}^{-1} \text{mol}^{-1})$
$\text{SO}_2(\text{g})$	248.1
$\text{O}_2(\text{g})$	205.3
$\text{SO}_3(\text{g})$	256.6



Free Energy (ΔG)

Free Energy	
▪	Thermodynamic favorability of the reaction
▪	Thermodynamically favorable ($-\Delta G^\circ$) or thermodynamically unfavorable ($+\Delta G^\circ$)
▪	Calculate:
▪	Table of standard values
▪	Hess's Law

Big Mamma Equation III: $\Delta G^\circ_{\text{rxn}} = \Sigma \Delta G^\circ_{\text{(products)}} - \Sigma \Delta G^\circ_{\text{(reactants)}}$

- ΔH° , ΔS° , and ΔG° may all be calculated from tables of standard values, from Hess' Law or from the Gibb's equation:

Connections to ΔH° and ΔS° :

Granddaddy of Them All: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

Caution on units: ΔH° and ΔG° are typically given in kJ mol^{-1} whereas ΔS° typically given as $\text{J K}^{-1}\text{mol}^{-1}$

Conditions of ΔG

ΔH	ΔS	ΔG
–	+	Spontaneous (–) at all temp
+	+	Spontaneous (–) at high temp
–	–	Spontaneous (–) at low temp
+	–	Non-spontaneous (+) at all temp

Free Energy, Equilibrium, and Cell Potential

ΔG°	K	E°
0	at equilibrium	0
negative	>1 , products favored	+
positive	<1 , reactants favored	–

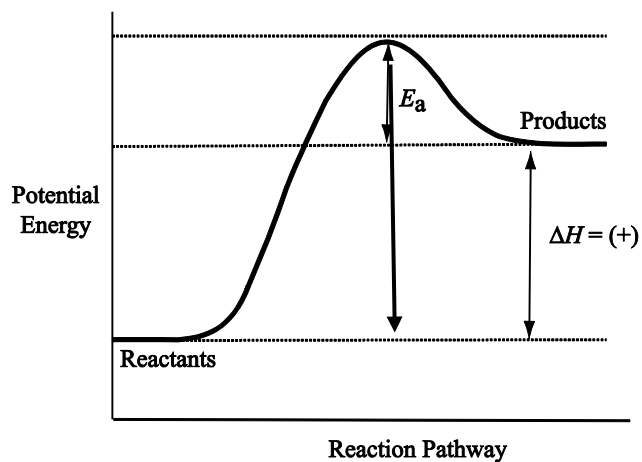
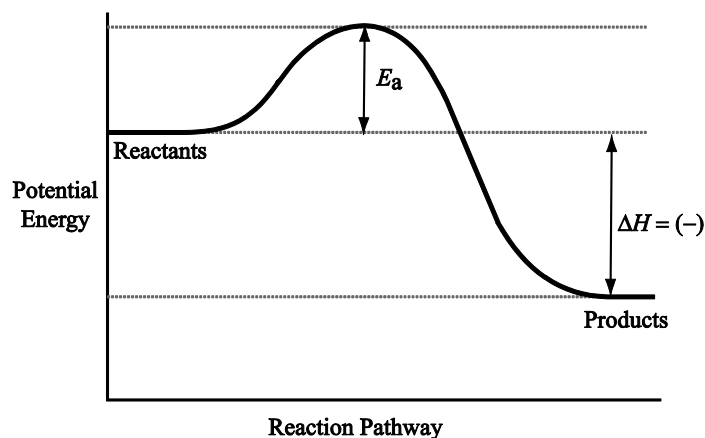
- Connecting ΔG° to K
 - $\Delta G^\circ = -RT \ln K$
- Connecting ΔG° to E
 - $\Delta G^\circ = -n \mathfrak{F} E^\circ$



Endothermic v. Exothermic

PROBLEM STRATEGY

You should be able to determine if the reactions are endothermic or exothermic and possibly determine the value of the ΔH° if the diagram has energy values given. For kinetics you will be asked to label the activation energy, E_a . CAUTION. Make sure to read carefully as questions are often asked about the *reverse* reaction.





Thermochemistry Cheat Sheet

Relationships

$q = mC_p\Delta T$	$\Delta G = \Delta H - T\Delta S$
$q = \Delta H$ (when pressure is constant/coffee cup)	$\Delta S_{\text{rxn}} = \sum \Delta S_{\text{prod}} - \sum \Delta S_{\text{react}}$
$(-) q_{\text{lost}} = q_{\text{gained}}$ (same value; opp. sign)	$\Delta G_{\text{rxn}} = \sum \Delta G_{\text{prod}} - \sum \Delta G_{\text{react}}$
$\Delta H_{\text{rxn}} = \sum \Delta H_{\text{prod}} - \sum \Delta H_{\text{react}}$	$\Delta G^\circ = -RT \ln K$ (use 8.31×10^{-3} kJ/molK for R) and watch your units for ΔG : they will be in kJ
$\Delta H_{\text{rxn}} = \sum \text{bonds}_{\text{broken}} - \sum \text{bonds}_{\text{formed}}$	$\Delta G^\circ = -n \mathfrak{F} E^\circ$ (96,500 for $\mathfrak{F}$)
$-\Delta H$ is exothermic; $+\Delta H$ is endothermic	$\Delta S = \frac{\Delta H}{T}$ at equilibrium (including phase change)
	$\Delta G = 0$ at equilibrium and direction change
Be cautious of which system component is losing heat and which is gaining heat. Assign +/- signs accordingly.	Use $\Delta G = \Delta H - T\Delta S$ equation to justify thermodynamic favorability. Discuss ΔH “overtaking” the $T\Delta S$ term and vice versa.

Connections

Kinetics – reaction diagrams Stoichiometry – Energy values are usually kJ/mol so if you have other than 1 mole adjust accordingly	Electrochem: $\Delta G = -n \mathfrak{F} E^\circ$ Equilibrium: $\Delta G = -RT \ln K$
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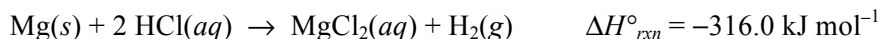
Potential Pitfalls

ΔH_{rxn} is usually in kJ mol ⁻¹ (that’s per mol of rxn) ΔH_f is usually in kJ mol ⁻¹ C_p = J/g°C (specific heat units)	ΔS is in J/K not in kJ like ΔH and ΔG ΔG must be negative for thermodynamic favorability Watch your signs and know what they mean
UNITS CAUTION: this calculation gives w in units of (L·atm) not Joules (or kJ)!!!! $1 \text{ atm} = 101,325 \frac{\text{N}}{\text{m}^2}$ and $1 \text{ L} = 0.001 \text{ m}^3$ $1 \text{ L} \cdot \text{atm} = 101.3 \text{ N} \cdot \text{m} = 101.3 \text{ J}$ ALL $P\Delta V$ calculations for work need to be $\times 101.3$ to convert to Joules, J	



NMSI Super Problem

Magnesium flakes were added to an open polystyrene cup filled with 50.0 mL of 1.00 M HCl solution. Assume the specific heat of the solution to be 4.18 J/g°C.



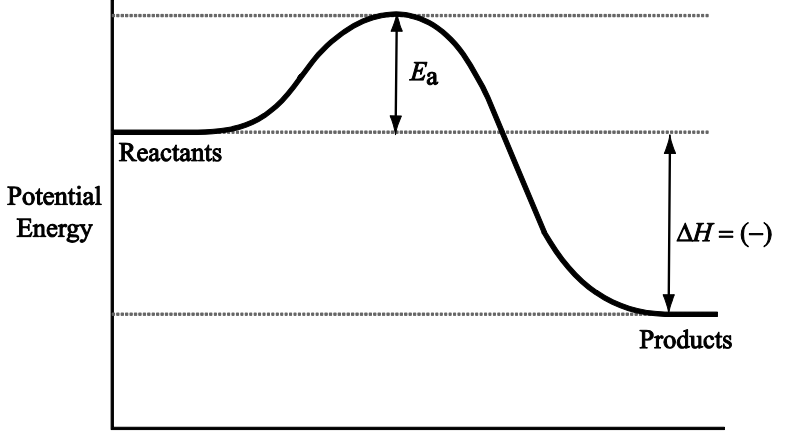
- (a) If 0.600 g of the magnesium were added, determine the total amount of heat released into the calorimeter.

$\text{heat released} = 316.0 \frac{\text{kJ}}{\text{mol}} \times \frac{0.600\text{g}}{24.31 \frac{\text{g}}{\text{mol}}} = 7.80 \text{ kJ}$	1 point is earned for calculating the number of moles of Mg reacted 1 point is earned for calculating the total amount of heat released
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- (b) Determine the temperature change in the calorimeter.

$q = mC\Delta T$ $7800 = (50.60)(4.18)(\Delta T)$ $36.9^\circ\text{C} = \Delta T$	1 point is earned for correctly calculating the ΔT consistent with part (a)
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- (c) Draw an energy diagram and label the enthalpy change, ΔH , for the reaction.

	1 point is earned for correctly sketching the energy diagram for an exothermic reaction. 1 point is earned for correctly labeling ΔH
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The hydrogen gas produced in the reaction of magnesium and HCl was captured and placed in a sealed container, which occupies a volume of 650 mL at a constant pressure of 1.0 atm. The temperature of the container and gas was changed by 15°C; the resulting volume of the gas in the container is 620 mL.

- (d) Is the temperature of the system increasing or decreasing. Justify your answer

The temperature of the system is decreasing. A decrease in the volume of gas indicates a decrease in the temperature of the gas since the system is at constant pressure and the amount of the gas is not changing.	1 point is earned for stating that the temperature will decrease, with correct justification.
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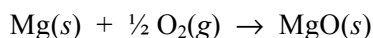
- (e) Is the statement in the box below correct? Justify your answer.

The gas collected in the container does work on the surroundings

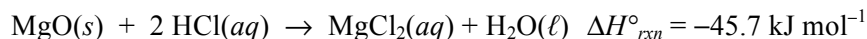
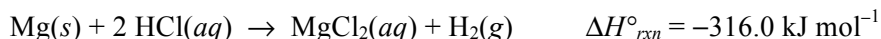
The statement is not correct. A decrease in the temperature will slow the particles, which will decrease the pressure in the system and cause the piston to move downward decreasing the volume of the container until the pressure inside and outside are equal. This indicates the surroundings are doing work on the system or gas.

1 point is earned for stating that statement is not correct with justification.

Answer the following questions about the oxidation of magnesium metal.



- (f) Determine the value of the standard enthalpy change for the reaction in the box above.



Using Hess's Law:		1 point is earned for correctly manipulating Equation 2 1 point is earned for correctly calculating the $\Delta H^\circ_{\text{rxn}}$ for the oxidation of magnesium
$\text{MgCl}_2(aq) + \text{H}_2\text{O}(\ell) \rightarrow \text{MgO}(s) + 2 \text{HCl}(aq)$	$\Delta H^\circ_{\text{rxn}} = +45.7 \text{ kJ mol}^{-1}$	
$\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(\ell)$	$\Delta H^\circ_{\text{rxn}} = -286 \text{ kJ mol}^{-1}$	
$\text{Mg}(s) + 2 \text{HCl}(aq) \rightarrow \text{MgCl}_2(aq) + \text{H}_2(g)$	$\Delta H^\circ_{\text{rxn}} = -316.0 \text{ kJ mol}^{-1}$	
$\text{Mg}(s) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{MgO}(s)$	$\Delta H^\circ_{\text{rxn}} = -556 \text{ kJ mol}^{-1}$	



- (g) Determine the value of the standard entropy change, $\Delta S^\circ_{\text{rxn}}$, for the oxidation of magnesium using the information in the following table.

Substance	S° (J mol ⁻¹ K ⁻¹)
Mg	33
O ₂	205
MgO	27

$\Delta S^\circ_{\text{rxn}} = \sum n\Delta S^\circ_{\text{products}} - \sum n\Delta S^\circ_{\text{reactants}}$ $\Delta S^\circ_{\text{rxn}} = [27] - [(33) + (\frac{1}{2} \times 205)] = -109 \text{ J mol}^{-1} \text{ K}^{-1}$	1 point is earned for multiplying the ΔS° of O₂ by it's coefficient ($\frac{1}{2}$) 1 point is earned for calculating the $\Delta S^\circ_{\text{rxn}}$
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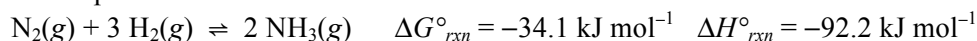
- (h) Calculate $\Delta G^\circ_{\text{rxn}}$ for the oxidation of magnesium at 25°C

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $\Delta G^\circ = [-556] - [(298)(-0.109)] = -524 \text{ kJ mol}^{-1}$	1 point is earned for correctly calculating the product $T\Delta S^\circ$ consistent with part (d) 1 point is earned for correctly substituting and calculating ΔG° consistent with part (c) and (d).
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- (i) Indicate whether the reaction is thermodynamically favored at 25°C. Justify your answer

Since ΔG° is negative the reaction is thermodynamically favored.	1 point is earned for correctly stating the reaction is thermodynamically favored with justification
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The hydrogen gas collected and placed in the sealed container above is mixed with nitrogen gas to produce ammonia according to the Haber process shown below.



- (j) In terms of the equilibrium constant, K , for the above reaction at 25°C

- i. Predict whether K will be greater than, less than, or equal to one. Justify your choice.

Since the reaction is spontaneous (ΔG° is negative) the equilibrium constant will be > 1 as the products are favored.	1 point is earned for the correct answer, with proper justification.
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- ii. Calculate its value.

$\Delta G^\circ = -RT \ln K_{\text{eq}}$ $\ln K_{\text{eq}} = -\frac{\Delta G^\circ}{RT} = -\frac{-34.1}{(8.31 \times 10^{-3})(298)} = 13.8$ $K_{\text{eq}} = e^{13.8} = 9.85 \times 10^5$	1 point is earned for the correct substitution, including converting the temperature to Kelvin. 1 point is earned for the correct answer. Note: If the previous answer is not rounded before calculating K, the acceptable answer of 9.56×10^5 is obtained.
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(k) In terms of the standard entropy change, ΔS°

i. Predict the sign of ΔS° for the above reaction. Justify your answer.

ΔS° will be negative as 4 mol of gas are converted into 2 mol of gas. The reaction is becoming less disordered.

1 point is earned for the correct sign, with proper justification.

ii. Calculate the value of $\Delta S^\circ_{\text{rxn}}$ for the above reaction at 25°C.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{(-92.2) - (-34.1)}{298} = -0.195 = -195 \text{ J mol}^{-1} \text{K}^{-1}$$

1 point is earned for correctly calculating the ΔS° consistent with part (b). Answer should be -195 (not -196).

(l) Using the data in the table below and the enthalpy of reaction, $\Delta H^\circ_{\text{rxn}}$, calculate the approximate bond energy of the nitrogen–hydrogen bond in ammonia.

Bonds	Approximate Bond Energy (kJ mol ⁻¹)
N — H	???
H — H	430
N ≡ N	960

$$\Delta H^\circ_{\text{rxn}} = \text{Sum of Bonds Broken} - \text{Sum of Bonds Formed}$$

$$-92.2 = [(1 \text{ N-N bond}) + (3 \text{ H-H bonds})] - [2(3 \text{ N-H bonds})]$$

$$-92.2 = [(960) + (3 \times 430)] - [6(\text{N-H bond})]$$

$$-92.2 = [2250] - [6(\text{N-H bond})]$$

$$2342 = 6(\text{N-H bond})$$

$$\text{N-H bond} = 390 \text{ kJ mol}^{-1}$$

1 point is earned for the correct number of bonds in all three compounds multiplied by the average bond enthalpies.

1 point for the correct N–H bond energy, with correct units.

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Question 5 (8 points)

Reaction	Equation	ΔH_{298}°	ΔS_{298}°	ΔG_{298}°
X	$\text{C}(s) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + \text{H}_2(g)$	+131 kJ mol ⁻¹	+134 J mol ⁻¹ K ⁻¹	+91 kJ mol ⁻¹
Y	$\text{CO}_2(g) + \text{H}_2(g) \rightleftharpoons \text{CO}(g) + \text{H}_2\text{O}(g)$	+41 kJ mol ⁻¹	+42 J mol ⁻¹ K ⁻¹	+29 kJ mol ⁻¹
Z	$2 \text{CO}(g) \rightleftharpoons \text{C}(s) + \text{CO}_2(g)$	?	?	?

Answer the following questions using the information related to reactions X, Y, and Z in the table above.

(a) For reaction X, write the expression for the equilibrium constant, K_p .

$K_p = \frac{p_{\text{CO}} \times p_{\text{H}_2}}{p_{\text{H}_2\text{O}}}$	One point is earned for the correct expression.
--	---

(b) For reaction X, will the equilibrium constant, K_p , increase, decrease, or remain the same if the temperature rises above 298 K? Justify your answer.

K_p will increase. If the temperature is increased for an endothermic reaction ($\Delta H_{298}^{\circ} = +131 \text{ kJ mol}^{-1}$), then by Le Chatelier's principle the reaction will shift toward products, thereby absorbing energy. With greater concentrations of products at equilibrium, the value of K_p will increase. OR Because $\Delta G^{\circ} = -RT \ln K_p = \Delta H_{298}^{\circ} - T \Delta S_{298}^{\circ}$, then $\ln K_p = -\frac{\Delta H_{298}^{\circ}}{RT} + \frac{\Delta S_{298}^{\circ}}{R}$. An increase in T for a positive ΔH_{298}° results in an increase in $\ln K_p$ and thus an increase in K_p.	One point is earned for the correct answer with appropriate justification.
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Question 5 (continued)

- (c) For reaction Y at 298 K, is the value of K_p greater than 1, less than 1, or equal to 1? Justify your answer.

K_p for reaction Y is less than 1. For reaction Y, $\Delta G_{298}^{\circ} = +29 \text{ kJ mol}^{-1}$, a positive number. Because $\Delta G^{\circ} = -RT \ln K$ and ΔG° is positive, then $\ln K_p$ must be negative. This is true when K_p is less than 1. OR A positive ΔG° results in a nonspontaneous reaction under standard conditions. This favors reactants over products as equilibrium is approached starting from standard conditions, resulting in a K_p less than 1.	One point is earned for the correct answer with appropriate justification.
--	---

- (d) For reaction Y at 298 K, which is larger: the total bond energy of the reactants or the total bond energy of the products? Explain.

The total bond energy of the reactants is larger. Reaction Y is endothermic ($\Delta H_{298}^{\circ} = +41 \text{ kJ mol}^{-1} > 0$), so there is a net input of energy as the reaction occurs. Thus, the total energy required to break the bonds in the reactants must be greater than the total energy released when the bonds are formed in the products.	One point is earned for the correct answer with appropriate explanation.
---	---

- (e) Is the following statement true or false? Justify your answer.

“On the basis of the data in the table, it can be predicted that reaction Y will occur more rapidly than reaction X will occur.”

The statement is false. Thermodynamic data for an overall reaction have no bearing on how slowly or rapidly the reaction occurs.	One point is earned for the correct answer with appropriate justification.
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Question 5 (continued)

(f) Consider reaction Z at 298 K.

(i) Is ΔS° for the reaction positive, negative, or zero? Justify your answer.

ΔS° for reaction Z is negative. In reaction Z, two moles of gas with relatively high entropy are converted into one mole of solid and one mole of gas, a net loss of one mole of gas and thus a net loss in entropy. OR Reaction Z can be obtained by reversing reactions X and Y and adding them together. Thus ΔS° for reaction Z is the sum of two negative numbers and must itself be negative.	One point is earned for the correct answer with an appropriate justification.
--	--

(ii) Determine the value of ΔH° for the reaction.

Add the values of the negatives of ΔH_{298}° for reactions X and Y : $-131 \text{ kJ mol}^{-1} + (-41 \text{ kJ mol}^{-1}) = \mathbf{-172 \text{ kJ mol}^{-1}}$	One point is earned for the correct answer.
--	--

(iii) A sealed glass reaction vessel contains only $\text{CO}(g)$ and a small amount of $\text{C}(s)$. If a reaction occurs and the temperature is held constant at 298 K, will the pressure in the reaction vessel increase, decrease, or remain the same over time? Explain.

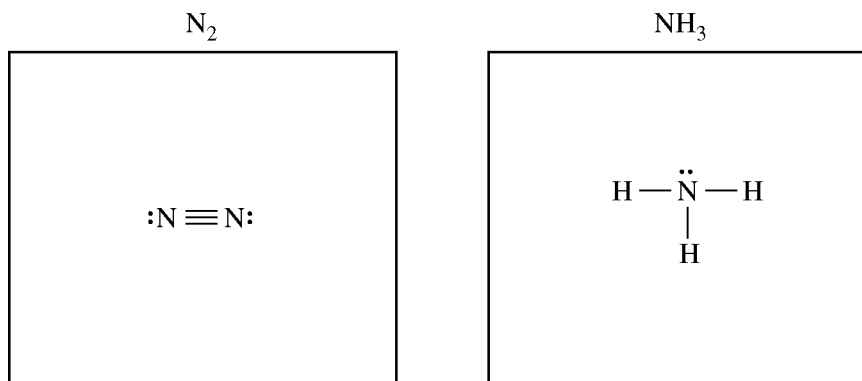
The pressure in the flask decreases. The reaction would proceed to the right, forming more $\text{C}(s)$ and $\text{CO}_2(g)$. Because two moles of $\text{CO}(g)$ would be consumed for every mole of $\text{CO}_2(g)$ that is produced, the total number of moles of gas in the flask would decrease, thereby causing the pressure in the flask to decrease.	One point is earned for the correct answer with an appropriate explanation.
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Question 5 (9 points)

Answer the following questions about nitrogen, hydrogen, and ammonia.

- (a) In the boxes below, draw the complete Lewis electron-dot diagrams for N_2 and NH_3 .



The correct structures are shown in the boxes above.	Two points are earned for the correct Lewis electron-dot diagrams (1 point each).
--	---

- (b) Calculate the standard free-energy change, ΔG° , that occurs when 12.0 g of $\text{H}_2(\text{g})$ reacts with excess $\text{N}_2(\text{g})$ at 298 K according to the reaction represented below.



$12.0 \text{ g H}_2 \times \frac{1 \text{ mol H}_2}{2.0 \text{ g H}_2} \times \frac{1 \text{ mol reaction}}{3 \text{ mol H}_2} \times \frac{-34 \text{ kJ}}{1 \text{ mol reaction}} = -68 \text{ kJ}$	One point is earned for the correct stoichiometry. One point is earned for the correct answer.
---	--

- (c) Given that ΔH_{298}° for the reaction is $-92.2 \text{ kJ mol}^{-1}$, which is larger, the total bond dissociation energy of the reactants or the total bond dissociation energy of the products? Explain.

$\Delta H_{298}^\circ = \Sigma (\text{bond energy of the reactants}) - \Sigma (\text{bond energy of the products})$ Based on the equation above, for ΔH_{298}° to be negative, the total bond energy of the products must be larger than the total bond energy of the reactants. OR More energy is released as product bonds are formed than is absorbed as reactant bonds are broken.	One point is earned for the correct answer with the correct equation and explanation.
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Question 5 (continued)

- (d) The value of the standard entropy change, ΔS_{298}° , for the reaction is $-199 \text{ J mol}^{-1}\text{K}^{-1}$. Explain why the value of ΔS_{298}° is negative.

All of the reactants and products in the reaction are in the gas phase, so the sign of the entropy change will depend on the number of moles of particles in the reactants and products. There are more moles of reactants (four) compared with moles of products (two), so there is a greater number of microstates in the reactants than in the products. Therefore the entropy decreases as the reaction proceeds (fewer possible microstates), and the sign of the entropy change is negative.	One point is earned for the correct explanation.
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- (e) Assume that ΔH° and ΔS° for the reaction are independent of temperature.

- (i) Explain why there is a temperature above 298 K at which the algebraic sign of the value of ΔG° changes.

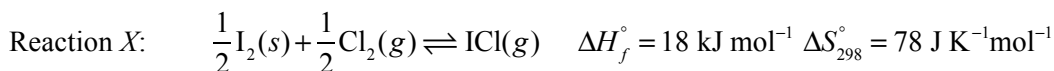
$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ As the temperature increases $T\Delta S^{\circ}$ will at some point exceed ΔH°. Because both ΔH° and ΔS° are negative, the sign of ΔG° will then change from negative to positive.	One point is earned for the correct explanation.
--	---

- (ii) Theoretically, the best yields of ammonia should be achieved at low temperatures and high pressures. Explain.

<u>Low temperatures:</u> The reaction is exothermic. By Le Chatelier's principle, decreasing the temperature drives the reaction to the right to produce more heat energy, and thus more ammonia is produced. <u>High pressures:</u> For this reaction, higher pressure is achieved by decreasing the volume of the container. As pressure increases, the reaction equilibrium shifts in the direction that reduces the total number of particles (by Le Chatelier's principle). In this case, the product has fewer moles of particles than the reactants; thus product would be favored. Higher pressure therefore results in an increase in the amount of ammonia.	One point is earned for explaining increased yield at low temperatures. One point is earned for explaining increased yield at high pressures.
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2006 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS (Form B)**Question 3 – Adapted into a Short Response question**

Answer the following questions about the thermodynamics of the reactions represented below.



- (a) Is reaction X, represented above, thermodynamically favored under standard conditions? Justify your answer.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $\Delta G^\circ = (18 \text{ kJ mol}^{-1}) - (298 \text{ K})(0.078 \text{ kJ K}^{-1}\text{mol}^{-1})$ $\Delta G^\circ = -5 \text{ kJ mol}^{-1}$ Reaction is thermodynamically favored since $\Delta G^\circ < 0$	1 point is earned for the correct value of ΔG° . 1 point is earned for correct justification of thermodynamic favorability.
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- (b) Calculate the value of the equilibrium constant, K_{eq} , for reaction X at 25°C.

$\Delta G^\circ = -RT \ln K$ $\ln K = -\frac{\Delta G^\circ}{RT} = -\frac{(-5 \text{ kJ mol}^{-1})}{(8.31 \times 10^{-3} \text{ kJ mol}^{-1}\text{K}^{-1})(298 \text{ K})} = 2.019$ $K = e^{2.019} = 8$	1 point is earned for the correct answer.
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- (c) What effect will an increase in temperature have on the equilibrium constant for reaction X? Explain your answer.

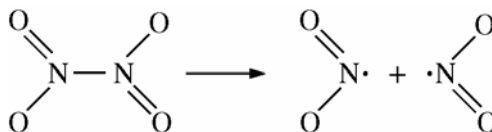
The reaction is endothermic ($\Delta H = +18 \text{ kJ mol}^{-1}$); an increase in temperature shifts the reaction to favor more products relative to the reactants, resulting in an increase in the value of K_{eq} .	1 point is earned for the correct response with a correct explanation.
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AP[®] CHEMISTRY
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Question 6

Use principles of thermodynamics to answer the following questions.

- (a) The gas N_2O_4 decomposes to form the gas NO_2 according to the equation below.



- (i) Predict the sign of ΔH° for the reaction. Justify your answer.

Bonds are broken when NO_2 molecules form from N_2O_4 molecules. Energy must be absorbed to break bonds, so the reaction is endothermic and the sign of ΔH° is positive.

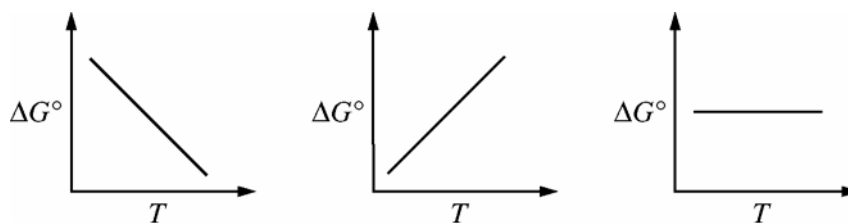
One point is earned for the correct sign and a correct explanation.

- (ii) Predict the sign of ΔS° for the reaction. Justify your answer.

There are two gaseous product molecules for each gaseous reactant molecule, so the product has more entropy than the reactant. The entropy increases as the reaction proceeds, so the sign of ΔS° is positive.

One point is earned for the correct sign and a correct explanation.

- (b) One of the diagrams below best represents the relationship between ΔG° and temperature for the reaction given in part (a). Assume that ΔH° and ΔS° are independent of temperature.



Draw a circle around the correct graph. Explain why you chose that graph in terms of the relationship $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$.

The leftmost graph should be circled.

ΔS° is positive, so as T increases, $T\Delta S^\circ$ becomes a larger positive number. At higher temperatures, you are subtracting larger positive numbers from ΔH° to get ΔG° , so ΔG° decreases with increasing temperature.

One point is earned for the correct graph selection.

One point is earned for the explanation.

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Question 6 (continued)

- (c) A reaction mixture of N_2O_4 and NO_2 is at equilibrium. Heat is added to the mixture while the mixture is maintained at constant pressure.

(i) Explain why the concentration of N_2O_4 decreases.

The reaction is endothermic. For endothermic reactions, increasing the temperature drives the reaction to the right. This increases the equilibrium concentration of NO_2 and decreases the equilibrium concentration of N_2O_4 .	One point is earned for the correct explanation.
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- (ii) The value of K_{eq} at 25°C is 5.0×10^{-3} . Will the value of K_{eq} at 100°C be greater than, less than, or equal to this value?

Because the reaction is endothermic, at higher temperatures the reaction goes further to the right. This means that the value of K_{eq} at 100°C will be greater than the value of K_{eq} at 25°C .	One point is earned for the correct choice. (No explanation required.)
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- (d) Using the value of K_{eq} at 25°C given in part (c)(ii), predict whether the value of ΔH° is expected to be greater than, less than, or equal to the value of $T\Delta S^\circ$. Explain.

K_{eq} at 25°C is less than 1, hence ΔG° must be positive. And in order for ΔG° to be positive, ΔH° must be greater than $T\Delta S^\circ$.	One point is earned for the correct prediction. One point is earned for the explanation.
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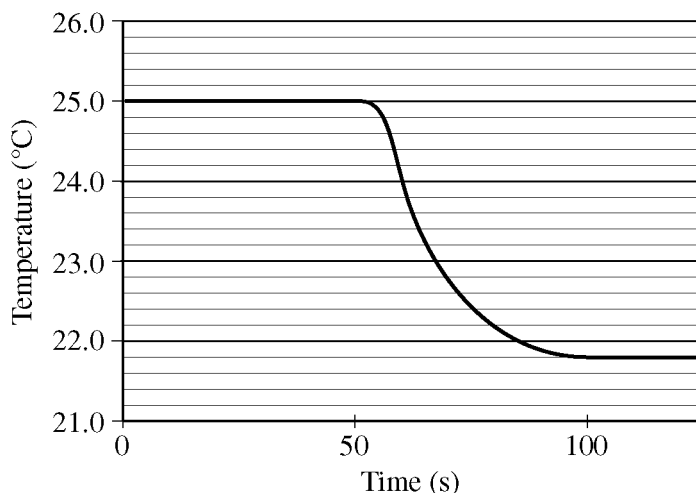
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Question 2

(10 points)

A student performs an experiment to determine the molar enthalpy of solution of urea, H_2NCONH_2 . The student places 91.95 g of water at 25°C into a coffee cup calorimeter and immerses a thermometer in the water. After 50 s, the student adds 5.13 g of solid urea, also at 25°C , to the water and measures the temperature of the solution as the urea dissolves. A plot of the temperature data is shown in the graph below.



- (a) Determine the change in temperature of the solution that results from the dissolution of the urea.

$\Delta T = 21.8 - 25.0 = -3.2$ Celsius degrees	One point is earned for the correct temperature change.
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- (b) According to the data, is the dissolution of urea in water an endothermic process or an exothermic process? Justify your answer.

The process is endothermic. The decrease in temperature indicates that the process for the dissolution of urea in water requires energy.	One point is earned for the correct choice with justification.
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Question 2 (continued)

- (c) Assume that the specific heat capacity of the calorimeter is negligible and that the specific heat capacity of the solution of urea and water is $4.2 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1}$ throughout the experiment.

- (i) Calculate the heat of dissolution of the urea in joules.

Assuming that no heat energy is lost from the calorimeter and given that the calorimeter has a negligible heat capacity, the sum of the heat of dissolution, q_{soln} and the change in heat energy of the urea-water mixture must equal zero. $q_{\text{soln}} + mc\Delta T = 0 \Rightarrow q_{\text{soln}} = -mc\Delta T$ $m_{\text{soln}} = 5.13 \text{ g} + 91.95 \text{ g} = 97.08 \text{ g}$ $q_{\text{soln}} = -(97.08 \text{ g})(4.2 \text{ J g}^{-1} \text{ }^{\circ}\text{C}^{-1})(-3.2^{\circ}\text{C}) = 1.3 \times 10^3 \text{ J}$	One point is earned for the correct setup. One point is earned for the correct numerical result for the heat of dissolution.
--	--

- (ii) Calculate the molar enthalpy of solution, $\Delta H_{\text{soln}}^{\circ}$, of urea in kJ mol^{-1} .

$\Delta H_{\text{soln}}^{\circ} = \frac{q_{\text{soln}}}{\text{mol solute}}$ molar mass of urea = $4(1.0) + 2(14.0) + 12.0 + 16.0 = 60.0 \text{ g mol}^{-1}$ moles of urea = $5.13 \text{ g urea} \times \frac{1 \text{ mol urea}}{60.0 \text{ g urea}} = 0.0855 \text{ mol}$ $\Delta H_{\text{soln}}^{\circ} = \frac{1.3 \times 10^3 \text{ J}}{0.0855 \text{ mol}} = 1.5 \times 10^4 \text{ J mol}^{-1} = 15 \text{ kJ mol}^{-1}$	One point is earned for the calculation of moles of urea. One point is earned for the correct numerical result with correct algebraic sign.
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- (d) Using the information in the table below, calculate the value of the molar entropy of solution, $\Delta S_{\text{soln}}^{\circ}$, of urea at 298 K. Include units with your answer.

	Accepted Value
$\Delta H_{\text{soln}}^{\circ}$ of urea	14.0 kJ mol^{-1}
$\Delta G_{\text{soln}}^{\circ}$ of urea	-6.9 kJ mol^{-1}

$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ $-6.9 \text{ kJ mol}^{-1} = 14.0 \text{ kJ mol}^{-1} - (298 \text{ K})(\Delta S^{\circ})$ $\Delta S_{\text{soln}}^{\circ} = 0.0701 \text{ kJ mol}^{-1} \text{ K}^{-1} = 70.1 \text{ J mol}^{-1} \text{ K}^{-1}$	One point is earned for the correct setup. One point is earned for the correct numerical result with correct units.
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Question 2 (continued)

- (e) The student repeats the experiment and this time obtains a result for ΔH_{soln}° of urea that is 11 percent below the accepted value. Calculate the value of ΔH_{soln}° that the student obtained in this second trial.

Error = $(0.11)(14.0 \text{ kJ mol}^{-1}) = 1.54 \text{ kJ mol}^{-1}$ $14.0 \text{ kJ mol}^{-1} - 1.54 \text{ kJ mol}^{-1} = 12.5 \text{ kJ mol}^{-1}$	One point is earned for the correct numerical result.
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- (f) The student performs a third trial of the experiment but this time adds urea that has been taken directly from a refrigerator at 5°C. What effect, if any, would using the cold urea instead of urea at 25°C have on the experimentally obtained value of ΔH_{soln}° ? Justify your answer.

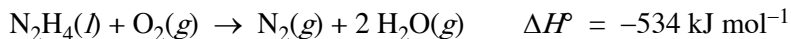
There would be an increase in the obtained value for ΔH_{soln}° because the colder urea would have caused a larger negative temperature change.	One point is earned for the correct prediction with justification.
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Question 5 - Modified for Short Free Response

Hydrazine is an inorganic compound with the formula N_2H_4 .

N_2H_4 reacts in air according to the equation below.



- (a) Is the reaction an oxidation-reduction, acid-base, or decomposition reaction? Justify your answer.

The reaction is an oxidation-reduction reaction. The oxidation state of N changes from -2 to 0 while that of O changes from 0 to -2 .

1 point is earned for the correct choice with a valid justification.

- (b) Predict the sign of the entropy change, ΔS , for the reaction. Justify your prediction.

The entropy change for the reaction is expected to be positive. There are three moles of gas produced from one mole of liquid and one mole of gas. The net increase of two moles of gas results in a greater entropy of products compared to the entropy of reactants.

1 point is earned for the correct prediction with a valid justification.

- (c) Indicate whether the statement written in the box below is true or false. Justify your answer.

The large negative ΔH° for the combustion of hydrazine results from the large release of energy that occurs when the strong bonds of the reactants are broken.

The statement is false on two counts. First, energy is released not when bonds are broken, but rather when they are formed. Second, the bonds in the reactants are relatively weak compared to the bonds in the products.

1 point is earned for correctly identifying the statement as false along with a valid justification.

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Modified for a Short Free Response

Question 5
(8 points)

Process	ΔH° (kJ/mol _{rxn})
$\text{Br}_2(l) \rightarrow \text{Br}_2(g)$	30.91
$\text{I}_2(s) \rightarrow \text{I}_2(g)$	62.44

At 298 K and 1 atm, the standard state of Br_2 is a liquid, whereas the standard state of I_2 is a solid. The enthalpy changes for the formation of $\text{Br}_2(g)$ and $\text{I}_2(g)$ from these elemental forms at 298 K and 1 atm are given in the table above.

- (a) Explain why ΔH° for the formation of $\text{I}_2(g)$ from $\text{I}_2(s)$ is larger than ΔH° for the formation of $\text{Br}_2(g)$ from $\text{Br}_2(l)$. In your explanation identify the type of particle interactions involved and a reason for the difference in magnitude of those interactions.

Two reasons may be given. The first reason is that London dispersion forces, the only intermolecular forces involved for both of these nonpolar molecules, will be stronger in I_2 because of its greater number of electrons and larger size. The second reason is that since ΔH of sublimation is approximately ΔH of fusion plus ΔH of vaporization, $\text{I}_2(g)$ should have a larger ΔH° of formation since it involves sublimation, whereas $\text{Br}_2(g)$ formation involves only vaporization.	1 point is earned for identifying London dispersion forces. 1 point is earned for either of the following: explaining the reason for the greater LDFs in I_2 OR stating that the enthalpy change from solid to gas is greater than the enthalpy change from liquid to gas.
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- (b) Predict which of the two processes shown in the table has the greater change in entropy. Justify your prediction.

$\text{I}_2(s) \rightarrow \text{I}_2(g)$ should have the greater change in entropy. The sublimation of I_2 may be thought of as a combination of fusion and vaporization. The conversion from solid to liquid would involve an increase in entropy, as would the conversion from liquid to gas. Br_2 is only undergoing the liquid to gas conversion and so will undergo a smaller entropy increase.	1 point is earned for the correct choice with a correct explanation.
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Question 5 (continued)

- (c) $\text{I}_2(s)$ and $\text{Br}_2(l)$ can react to form the compound $\text{IBr}(l)$. Predict which would have the greater molar enthalpy of vaporization, $\text{IBr}(l)$ or $\text{Br}_2(l)$. Justify your prediction.

$\text{IBr}(l)$. Two reasons may be given. First, IBr is polar, and dipole-dipole forces would tend to increase the enthalpy of vaporization. Second, IBr should have stronger London dispersion forces because of the greater number of electrons in the larger IBr molecule.	1 point is earned for the correct choice with either or both of the acceptable reasons.
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