

NATIONAL MATH + SCIENCE INITIATIVE

AP CHEMISTRY

Thermodynamics

2016 EDITION

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https://www.surveymonkey.com/r/S_SSS



Periodic Table of the Elements

1 H 1.0079																	2 He 4.0026
3 Li 6.941	4 Be 9.012															9 F 19.00	10 Ne 20.179
11 Na 22.99	12 Mg 24.30															17 Cl 35.453	18 Ar 39.948
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.938	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 72.59	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 93.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.91	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 *La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.2	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.02	89 †Ac 227.03	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 § (269)	111 § (272)	112 § (277)	§Not yet named					

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.4	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	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 (260)

*Lanthanide Series:

†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 atm = 760 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

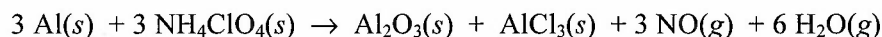
Enthalpy (ΔH)

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: $\Delta H^\circ_{\text{rxn}} = \sum \Delta H^\circ_{\text{f(products)}} - \sum \Delta H^\circ_{\text{f(reactants)}}$

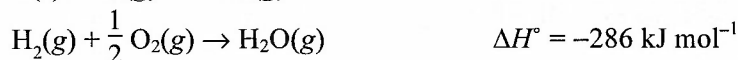
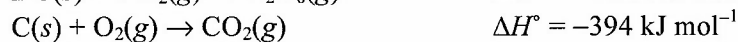
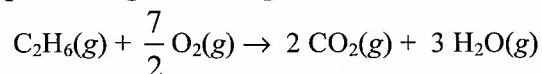


Substance	ΔH_f° (kJ/mol)
$\text{NH}_4\text{ClO}_4(s)$	–295
$\text{Al}_2\text{O}_3(s)$	–1676
$\text{AlCl}_3(s)$	–704
$\text{NO}(g)$	90.0
$\text{H}_2\text{O}(g)$	–242



Hess's Law

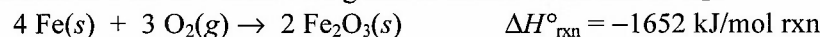
- Enthalpy is not dependent on the reaction pathway. If you can find a combination of chemical equations that add up to the desired *overall* equation, you can sum up the ΔH_{rxn} 's for the individual reactions to get the overall ΔH_{rxn} .
- Remember this:
 - First decide how to rearrange equations 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 ?



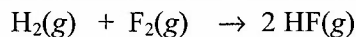
$$\text{heat released} = \frac{-1652 \text{ kJ}}{4 \text{ mol Fe}} \times \frac{1.00 \text{ g}}{55.85 \frac{\text{g}}{\text{mol}}} = -7.39 \text{ kJ per gram of Fe}$$

- 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° ($\text{J K}^{-1} \text{mol}^{-1}$)
$\text{SO}_2(\text{g})$	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

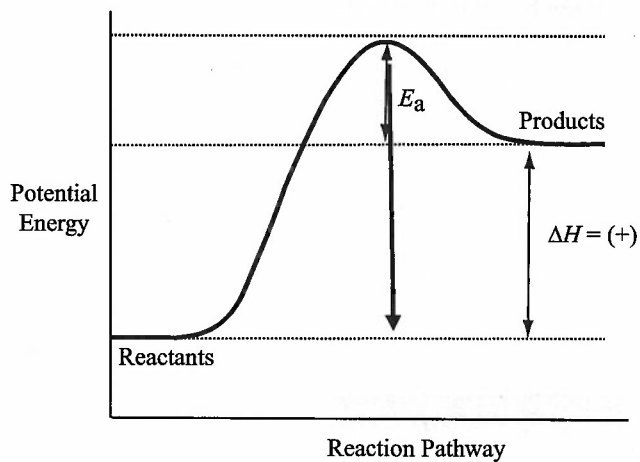
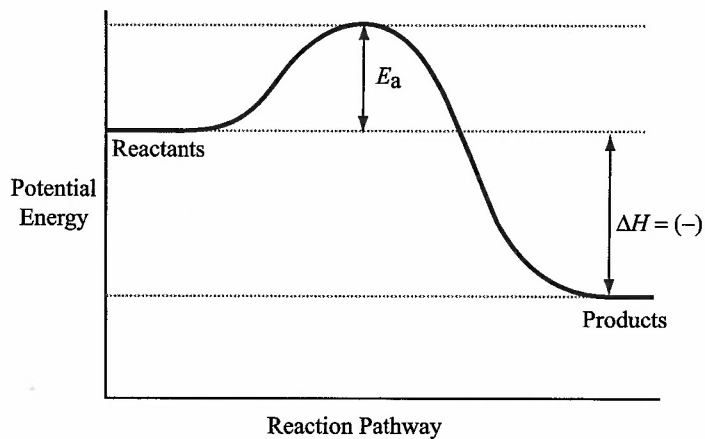
Free Energy, Equilibrium, and Cell Potential

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
 - $\Delta G^\circ = -n \mathcal{F} E^\circ$


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
$\Delta H_{\text{rxn}} = \sum \text{bonds}_{\text{broken}} - \sum \text{bonds}_{\text{formed}}$	$\Delta G^\circ = -n\mathfrak{S} E^\circ$ (96,500 for \mathfrak{S})
$-\Delta H$ 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: $\Delta G = -n\mathfrak{S} E^\circ$ Equilibrium: $\Delta G = -RT\ln K$
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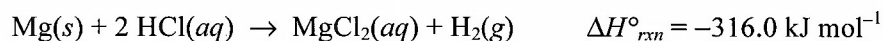
Potential Pitfalls

ΔH_{rxn} is usually in kJ mol ⁻¹ (that's per mol of rxn) ΔH_f° is usually in kJ mol ⁻¹ $C_p = \text{J/g}^\circ\text{C}$ (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.



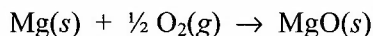
- If 0.600 g of the magnesium were added, determine the total amount of heat released into the calorimeter.
- Determine the temperature change in the calorimeter.
- Draw an energy diagram and label the enthalpy change, ΔH , for the reaction.

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.

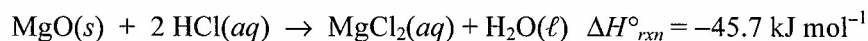
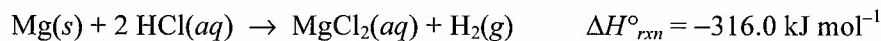
- Is the temperature of the system increasing or decreasing. Justify your answer
- Is the statement in the box below correct? Justify your answer.

The gas collected in the container does work on the surroundings

Answer the following questions about the oxidation of magnesium metal.



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



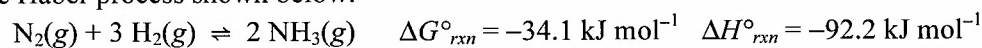
- Determine the value of the standard entropy change, ΔS°_{rxn} , for the oxidation of magnesium using the information in the following table.

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



- (h) Calculate $\Delta G^\circ_{\text{rxn}}$ for the oxidation of magnesium at 25°C
- (i) Indicate whether the reaction is thermodynamically favored at 25°C . Justify your answer

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
- Predict whether K will be greater than, less than, or equal to one. Justify your choice.
 - Calculate its value.
- (k) In terms of the standard entropy change, ΔS°
- Predict the sign of ΔS° for the above reaction. Justify your answer.
 - Calculate the value of $\Delta S^\circ_{\text{rxn}}$ for the above reaction at 25°C .
- (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

2009 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS

Answer Question 5 and Question 6. The Section II score weighting for these questions is 15 percent each.

Your responses to these questions will be graded on the basis of the accuracy and relevance of the information cited. Explanations should be clear and well organized. Examples and equations may be included in your responses where appropriate. Specific answers are preferable to broad, diffuse responses.

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	$2 \text{CO}(g) \rightleftharpoons \text{C}(s) + \text{CO}_2(g)$?	?	?

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

- For reaction X, write the expression for the equilibrium constant, K_p .
- 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.
- 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.
- 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.
- 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."
- Consider reaction Z at 298 K.
 - Is ΔS° for the reaction positive, negative, or zero? Justify your answer.
 - Determine the value of ΔH° for the reaction.
 - A sealed glass reaction vessel contains only CO(g) and a small amount of 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.

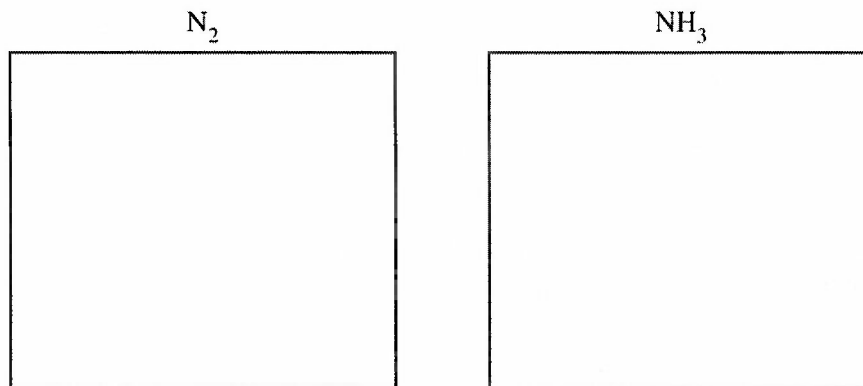
2009 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS (Form B)

Answer Question 5 and Question 6. The Section II score weighting for these questions is 15 percent each.

Your responses to these questions will be graded on the basis of the accuracy and relevance of the information cited. Explanations should be clear and well organized. Examples and equations may be included in your responses where appropriate. Specific answers are preferable to broad, diffuse responses.

5. 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 .



(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.



(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.

(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.

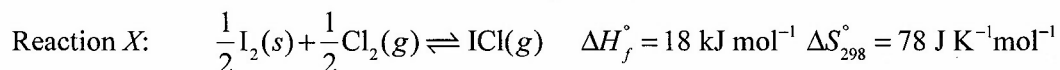
(e) Assume that ΔH° and ΔS° for the reaction are independent of temperature.

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

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

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.

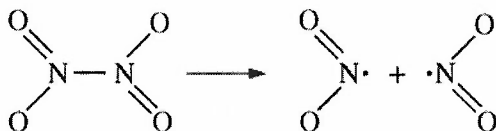


- Is reaction *X*, represented above, thermodynamically favored under standard conditions? Justify your answer.
- Calculate the value of the equilibrium constant, K_{eq} , for reaction *X* at 25°C.
- What effect will an increase in temperature have on the equilibrium constant for reaction *X*? Explain your answer.

2008 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS (Form B)

6. Use principles of thermodynamics to answer the following questions.

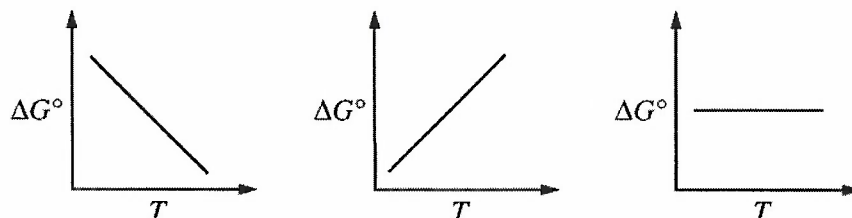
(a) The gas N_2O_4 decomposes to form the gas NO_2 according to the equation below.



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

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

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

(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.

(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?

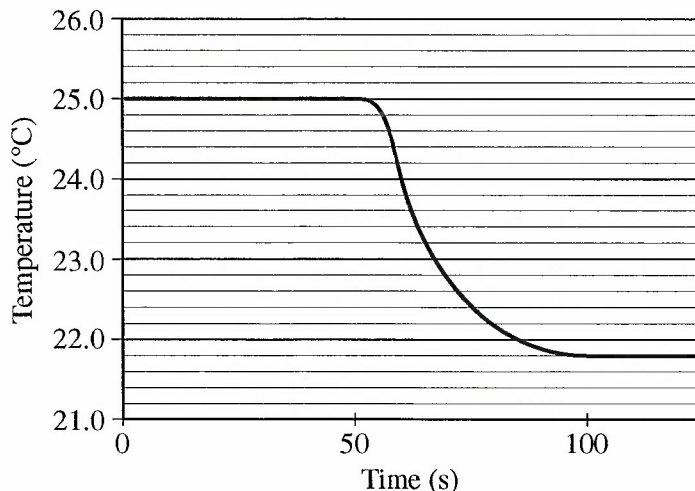
(d) Using the value of K_{eq} at 25°C given in part (c)(ii), predict whether the value of ΔH° is expected to be greater than, less than, or equal to the value of $T\Delta S^\circ$. Explain.

STOP

END OF EXAM

2010 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS

2. 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.
- (b) According to the data, is the dissolution of urea in water an endothermic process or an exothermic process? Justify your answer.
- (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.
- Calculate the heat of dissolution of the urea in joules.
 - Calculate the molar enthalpy of solution, $\Delta H_{\text{soln}}^\circ$, of urea in kJ mol^{-1} .
- (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}

- (e) The student repeats the experiment and this time obtains a result for $\Delta H_{\text{soln}}^\circ$ of urea that is 11 percent below the accepted value. Calculate the value of $\Delta H_{\text{soln}}^\circ$ that the student obtained in this second trial.
- (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 $\Delta H_{\text{soln}}^\circ$? Justify your answer.

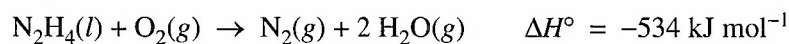
2011 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS

Modified for a Short Free Response

Your responses to these questions will be scored on the basis of the accuracy and relevance of the information cited. Explanations should be clear and well organized. Examples and equations may be included in your responses where appropriate. Specific answers are preferable to broad, diffuse responses.

5. 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.
- (b) Predict the sign of the entropy change, ΔS , for the reaction. Justify your prediction.
- (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.

2012 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS

Modified for a Short Free Response

Your responses to these questions will be scored on the basis of the accuracy and relevance of the information cited. Explanations should be clear and well organized. Examples and equations may be included in your responses where appropriate. Specific answers are preferable to broad, diffuse responses.

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

5. 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.
- (b) Predict which of the two processes shown in the table has the greater change in entropy. Justify your prediction.
- (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.