

# Chemistry

## Enthalpy, Entropy and Free Energy



The bankruptcy sale at the Entropy Institute was going to more difficult than Dave thought it'd be.



# 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						

*Lanthanide Series:		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
†Actinide Series:		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)

# 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)

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## ATOMIC STRUCTURE

$$E = h\nu$$

$$c = \lambda\nu$$

$E$  = energy

$\nu$  = frequency

$\lambda$  = wavelength

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

Speed of light,  $c = 2.998 \times 10^8$  m s<sup>-1</sup>

Avogadro's number =  $6.022 \times 10^{23}$  mol<sup>-1</sup>

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

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## 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)

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## 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

$S^\circ$  = standard entropy

$H^\circ$  = standard enthalpy

$G^\circ$  = standard free energy

$n$  = number of moles

$E^\circ$  = standard reduction potential

$I$  = current (amperes)

$q$  = charge (coulombs)

$t$  = time (seconds)

Faraday's constant,  $F = 96,485$  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 ( $\Delta H$ ); specific heat ( $C_p$ ); endothermic; exothermic; heat ( $q$ ); heat capacity ( $C$ ); heat transfer; bond energy; entropy ( $\Delta S$ ); Gibb's free energy ( $\Delta G$ ); 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 ( $\Delta H$ )	Energy content	+ endothermic	- exothermic
Entropy ( $\Delta S$ )	Disorder	+ increase in the dispersal of matter	- decrease in the dispersal of matter
Free energy ( $\Delta G$ )	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 ( $\Delta E$ ) 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  $\Delta V$  (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)
- $\Delta T$  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°C)
- $m$  = mass in grams
- the specific heat of water (liquid) = 4.184 J/g°C

Also note:

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

### Enthalpy ( $\Delta H$ )

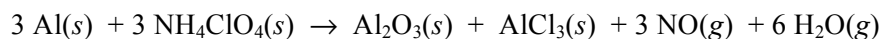
#### Enthalpy

- |                                                                                                                                                                                                                                                                                                                                                                                                                                 |
|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <ul style="list-style-type: none"> <li>Heat content; <math>\Delta H</math></li> <li>Endothermic (+) or Exothermic (-)</li> <li>Calculating Enthalpy 5 Ways               <ul style="list-style-type: none"> <li>Calorimetry (see above)</li> <li>Enthalpy of formation, <math>\Delta H_f^\circ</math> (using table of standard values)</li> <li>Hess's Law</li> <li>Stoichiometry</li> <li>Bond Energies</li> </ul> </li> </ul> |
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### $\Delta H_f^\circ$ – Enthalpy of Formation

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

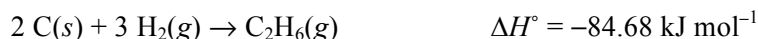
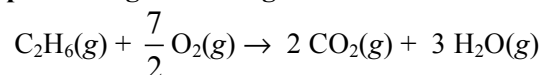
**Big Mamma Equation:**  $\Delta H^\circ_{\text{rxn}} = \Sigma \Delta H^\circ_{\text{f(products)}} - \Sigma \Delta H^\circ_{\text{f(reactants)}}$



Substance	$\Delta H_f^\circ$ (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

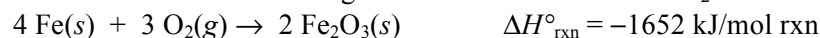
- Enthalpy is not dependent on the reaction pathway. If you can find a combination of chemical equations that add up to the desired *overall* equation, you can sum up the  $\Delta H_{\text{rxn}}$ 's for the individual reactions to get the overall  $\Delta H_{\text{rxn}}$ .
- Remember this:
  - First 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  $\Delta H$
  - If equations had to be multiplied to get a correct coefficient, multiply the  $\Delta H$  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 $\Delta H$

- 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  $\text{O}_2$ ?



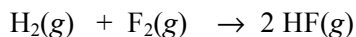
$$\text{heat released} = \frac{-1652 \text{ kJ}}{4 \text{ mol Fe}} \times \frac{1.00 \text{ g}}{55.85 \frac{\text{g}}{\text{mol}}} = -7.39 \text{ kJ per gram of Fe}$$

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

### Using Bond Energy to Calculate $\Delta H$

- 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 ( $\Delta S$ )

### 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 ( $\Delta G$ )

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:**  $\Delta G^\circ_{\text{rxn}} = \Sigma \Delta G^\circ_{\text{(products)}} - \Sigma \Delta G^\circ_{\text{(reactants)}}$

- $\Delta H^\circ$ ,  $\Delta S^\circ$ , and  $\Delta G^\circ$  may all be calculated from tables of standard values, from Hess' Law or from the Gibb's equation:

Connections to  $\Delta H^\circ$  and  $\Delta S^\circ$ :

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

Caution on units:  $\Delta H^\circ$  and  $\Delta G^\circ$  are typically given in  $\text{kJ mol}^{-1}$  whereas  $\Delta S^\circ$  typically given as  $\text{J K}^{-1}\text{mol}^{-1}$

### Conditions of $\Delta G$

$\Delta H$	$\Delta S$	$\Delta G$
-	+	Spontaneous (-) at all temp
+	+	Spontaneous (-) at high temp
-	-	Spontaneous (-) at low temp
+	-	Non-spontaneous (+) at all temp

### Free Energy, Equilibrium, and Cell Potential

$\Delta G^\circ$	$K$	$E^\circ$
0	at equilibrium	0
negative	>1, products favored	+
positive	<1, reactants favored	-

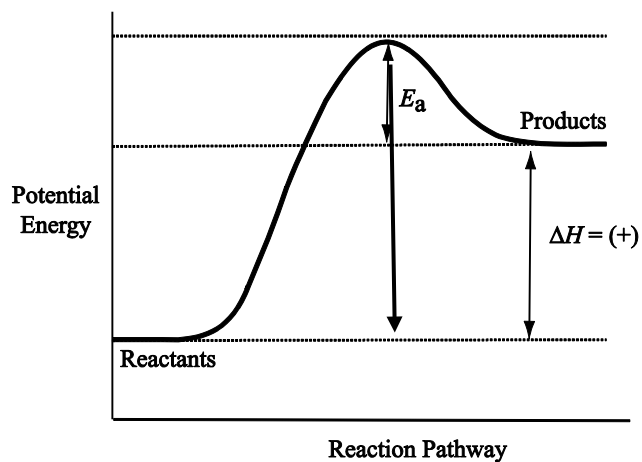
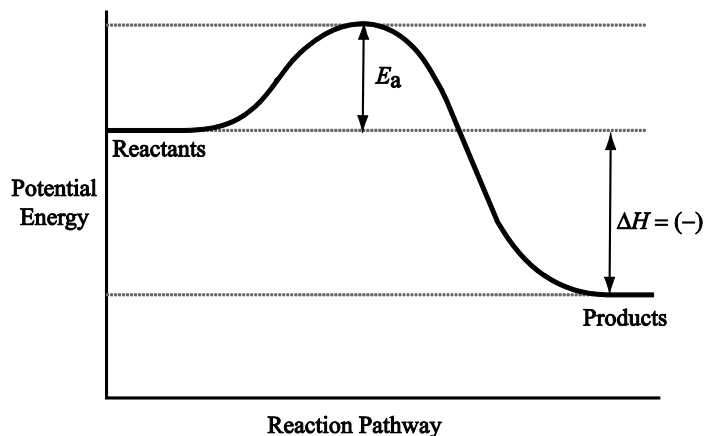
- Connecting  $\Delta G^\circ$  to  $K$ 
  - $\Delta G^\circ = -RT \ln K$
- Connecting  $\Delta G^\circ$  to  $E$ 
  - $\Delta G^\circ = -n \mathcal{F} E^\circ$



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  $\Delta H^\circ$  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 $8.31 \times 10^{-3}$ kJ/molK for $R$ ) and watch your units for $\Delta G$ : 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 $\Delta H$ "overtaking" the $T\Delta S$ term and vice versa.

### Connections

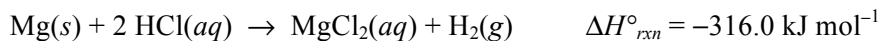
Kinetics – reaction diagrams Stoichiometry – Energy values are usually kJ/mol so if you have other than 1 mole adjust accordingly	Electrochem: $\Delta G = -n \mathfrak{F} E^\circ$ Equilibrium: $\Delta G = -RT \ln K$
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### Potential Pitfalls

$\Delta H_{\text{rxn}}$ is usually in kJ mol <sup>-1</sup> (that's per mol of rxn) $\Delta H_f$ is usually in kJ mol <sup>-1</sup> $C_p = \text{J/g}^\circ\text{C}$ (specific heat units)	$\Delta S$ is in J/K not in kJ like $\Delta H$ and $\Delta G$ $\Delta G$ 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.

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

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

	<p><b>1 point</b> is earned for correctly sketching the energy diagram for an exothermic reaction.</p> <p><b>1 point</b> is earned for correctly labeling <math>\Delta H</math></p>
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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

<p>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.</p>	<p><b>1 point</b> is earned for stating that the temperature will decrease, with correct justification.</p>
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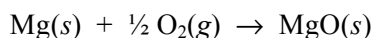
(e) Is the statement in the box below correct? Justify your answer.

The gas collected in the container does work on the surroundings

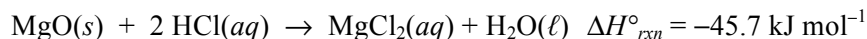
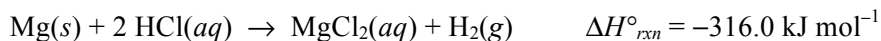
The statement is not correct. A decrease in the temperature will slow the particles, which will decrease the pressure in the system and cause the piston to move downward decreasing the volume of the container until the pressure inside and outside are equal. This indicates the surroundings are doing work 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:		<b>1 point</b> is earned for correctly manipulating Equation 2
$\text{MgCl}_2(aq) + \text{H}_2\text{O}(\ell) \rightarrow \text{MgO}(s) + 2 \text{HCl}(aq)$	$\Delta H^\circ_{rxn} = +45.7 \text{ kJ mol}^{-1}$	<b>1 point</b> is earned for correctly calculating the $\Delta H^\circ_{rxn}$ for the oxidation of magnesium
$\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(\ell)$	$\Delta H^\circ_{rxn} = -286 \text{ kJ mol}^{-1}$	
$\text{Mg}(s) + 2 \text{HCl}(aq) \rightarrow \text{MgCl}_2(aq) + \text{H}_2(g)$	$\Delta H^\circ_{rxn} = -316.0 \text{ kJ mol}^{-1}$	
$\text{Mg}(s) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{MgO}(s)$	$\Delta H^\circ_{rxn} = -556 \text{ kJ mol}^{-1}$	



- (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	$S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
Mg	33
O <sub>2</sub>	205
MgO	27

$\Delta S^\circ_{\text{rxn}} = \sum n \Delta S^\circ_{\text{products}} - \sum n \Delta S^\circ_{\text{reactants}}$ $\Delta S^\circ_{\text{rxn}} = [27] - [(33) + (\frac{1}{2} \times 205)] = -109 \text{ J mol}^{-1} \text{ K}^{-1}$	<p><b>1 point</b> is earned for multiplying the <math>\Delta S^\circ</math> of O<sub>2</sub> by it's coefficient (½)</p> <p><b>1 point</b> is earned for calculating the <math>\Delta S^\circ_{\text{rxn}}</math></p>
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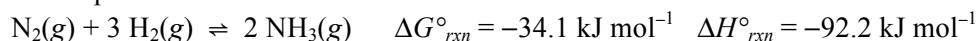
- (h) Calculate  $\Delta G^\circ_{\text{rxn}}$  for the oxidation of magnesium at 25°C

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

<p>Since <math>\Delta G^\circ</math> is negative the reaction is thermodynamically favored.</p>	<p><b>1 point</b> is earned for correctly stating the reaction is thermodynamically favored with justification</p>
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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.

<p>Since the reaction is spontaneous (<math>\Delta G^\circ</math> is negative) the equilibrium constant will be <math>&gt; 1</math> as the products are favored.</p>	<p><b>1 point</b> is earned for the correct answer, with proper justification.</p>
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- ii. Calculate its value.

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

i. Predict the sign of  $\Delta S^\circ$  for the above reaction. Justify your answer.

$\Delta S^\circ$ will be negative as 4 mol of gas are converted into 2 mol of gas. The reaction is becoming less disordered.	<b>1 point</b> is earned for the correct sign, with proper justification.
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ii. Calculate the value of  $\Delta S^\circ_{rxn}$  for the above reaction at 25°C.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ $\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{(-92.2) - (-34.1)}{298} = -0.195 = -195 \text{ J mol}^{-1}\text{K}^{-1}$	<b>1 point</b> is earned for correctly calculating the $\Delta S^\circ$ consistent with part (b). Answer should be -195 (not -196).
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(l) Using the data in the table below and the enthalpy of reaction,  $\Delta H^\circ_{rxn}$ , calculate the approximate bond energy of the nitrogen–hydrogen bond in ammonia.

Bonds	Approximate Bond Energy (kJ mol <sup>-1</sup> )
N—H	???
H—H	430
N≡N	960

$\Delta H^\circ_{rxn} = \text{Sum of Bonds Broken} - \text{Sum of Bonds Formed}$ $-92.2 = [(1 \text{ N-N bond}) + (3 \text{ H-H bonds})] - [2(3 \text{ N-H bonds})]$ $-92.2 = [(960) + (3 \times 430)] - [6(\text{N-H bond})]$ $-92.2 = [2250] - [6(\text{N-H bond})]$ $2342 = 6(\text{N-H bond})$ $\text{N-H bond} = 390 \text{ kJ mol}^{-1}$	<p><b>1 point</b> is earned for the correct number of bonds in all three compounds multiplied by the average bond enthalpies.</p> <p><b>1 point</b> for the correct N–H bond energy, with correct units.</p>
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