

# NATIONAL MATH + SCIENCE INITIATIVE

**AP CHEMISTRY**

Thermochemistry

2016 EDITION

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# 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  
 $\nu$  = 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

## 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

## THERMOCHEMISTRY

### 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

### 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 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

$$\Delta T = T_f - T_i \quad (\text{final} - \text{initial})$$

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

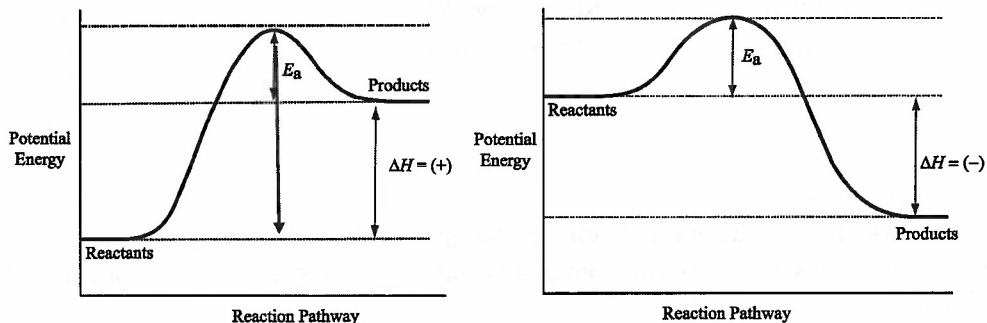
the specific heat of water (liquid) =  $4.184 J/g^\circ C$

Also note:

$$q = -\Delta H \quad \text{at constant pressure}$$

**Enthalpy ( $\Delta H$ )**

- Think of enthalpy as a change in heat content;  $\Delta H$
- The change can be either Endothermic (+) or Exothermic (-)
  - 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.

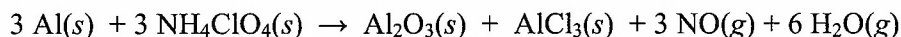


- There are at least 5 ways you might be asked to calculate enthalpy:
  - Calorimetry (see above)
  - Enthalpy of formation,  $\Delta H_f^\circ$  (using table of standard values)
  - Hess's Law
  - Stoichiometry
  - Bond Energies

 **$\Delta H_f^\circ$ — 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

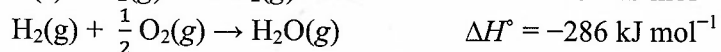
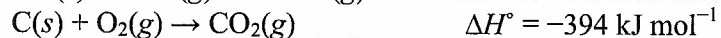
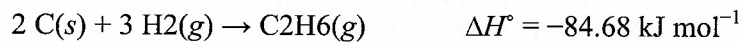
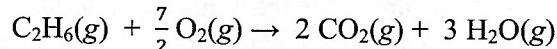
**Big Mamma Equation:**  $\Delta H^\circ_{\text{rxn}} = \Sigma \Delta H^\circ_f (\text{products}) - \Sigma \Delta H^\circ_f (\text{reactants})$



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**

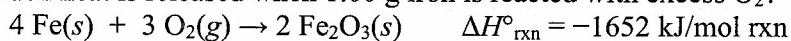
- Enthalpy is not dependent on the reaction pathway. If you can find a combination of chemical equations that add up to the desired overall equation, you can sum up the  $\Delta H_{\text{rxn}}$ 's for the individual reactions to get the overall  $\Delta H_{\text{rxn}}$ .
- Remember this:
  - First decide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



### 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  $\text{O}_2$ ?



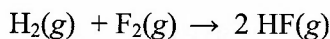
$$\text{heat released} = 1.00 \text{ g} \times \frac{1 \text{ mol}}{55.0 \text{ g}} \times \frac{-1652 \text{ kJ}}{4 \text{ mol Fe}} = 7.39 \text{ kJ per gram of Fe}$$

- 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

## THERMOCHEMISTRY CHEAT SHEET

### Relationships

$$q = mC_p\Delta T$$

$$q = \Delta H \text{ (when pressure is constant/coffee cup)}$$

$$(-) q_{\text{lost}} = q_{\text{gained}} \text{ (same value; opp. sign)}$$

$$\Delta H_{\text{rxn}} = \sum \Delta H_{\text{prod}} - \sum \Delta H_{\text{react}}$$

$$\Delta H_{\text{rxn}} = \sum \text{bonds broken} - \sum \text{bonds formed}$$

$-\Delta H$  is exothermic;  $+\Delta H$  is endothermic

### Connections

Be cautious of which system component is losing heat and which is gaining heat.  
Assign +/- signs accordingly.

Kinetics – reaction diagrams

Stoichiometry – Energy values are usually kJ/mol so if you have other than 1 mole adjust accordingly

Thermodynamics – most often  $\Delta H$  are just one part of a larger problem involving  $\Delta S$  and  $\Delta G$ .  
Especially using the equation  $\Delta G = \Delta H - T\Delta S$

### Potential Pitfalls

$\Delta H_{\text{rxn}}$  is usually in  $\text{kJ mol}^{-1}$  (that's per mol of rxn)

$\Delta H_f$  is usually in  $\text{kJ mol}^{-1}$

$C_p = \text{J/g}^\circ\text{C}$  (specific heat units)

UNITS CAUTION: this calculation gives  $w$  in units of (L·atm) not Joules (or kJ)!!!!

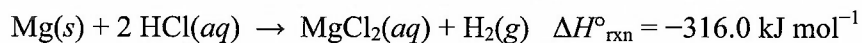
$$1 \text{ atm} = 101,325 \text{ N/m}^2 \text{ and } 1 \text{ L} = 0.001 \text{ m}^3$$

$$1 \text{ L}\cdot\text{atm} = 101.3 \text{ N}\cdot\text{m} = 101.3 \text{ J}$$

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.
- (b) Determine the temperature change in the calorimeter.
- (c) Draw an energy diagram and label the enthalpy change,  $\Delta H$ , for the reaction.

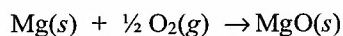
The hydrogen gas produced in the reaction of magnesium and HCl was captured and placed in a sealed container, which occupies a volume of 650 mL at a constant pressure of 1.0 atm. The temperature of the container and gas was changed by 15°C; the resulting volume of the gas in the container is 620 mL.

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

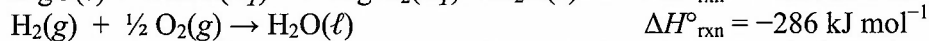
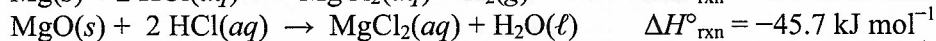
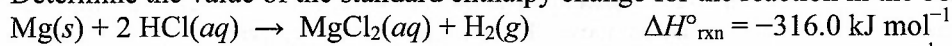
The gas collected in the container does work on the surroundings



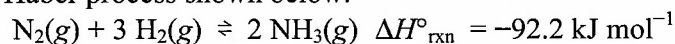
Answer the following questions about the oxidation of magnesium metal.



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

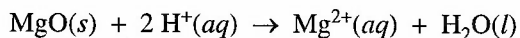


The hydrogen gas collected and placed in the sealed container above is mixed with nitrogen gas to produce ammonia according to the Haber process shown below.



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 ( $\text{kJ mol}^{-1}$ )
N–H	???
H–H	430
$\text{N}\equiv\text{N}$	960

2013 AP<sup>®</sup> CHEMISTRY FREE-RESPONSE QUESTIONS

3. A student was assigned the task of determining the enthalpy change for the reaction between solid MgO and aqueous HCl represented by the net-ionic equation above. The student uses a polystyrene cup calorimeter and performs four trials. Data for each trial are shown in the table below.

Trial	Volume of 1.0 M HCl (mL)	Mass of MgO(s) Added (g)	Initial Temperature of Solution (°C)	Final Temperature of Solution (°C)
1	100.0	0.25	25.5	26.5
2	100.0	0.50	25.0	29.1
3	100.0	0.25	26.0	28.1
4	100.0	0.50	24.1	28.1

- (a) Which is the limiting reactant in all four trials, HCl or MgO? Justify your answer.
- (b) The data in one of the trials is inconsistent with the data in the other three trials. Identify the trial with inconsistent data and draw a line through the data from that trial in the table above. Explain how you identified the inconsistent data.

For parts (c) and (d), use the data from one of the other three trials (i.e., not from the trial you identified in part (b) above). Assume the calorimeter has a negligible heat capacity and that the specific heat of the contents of the calorimeter is  $4.18 \text{ J}/(\text{g} \cdot \text{C}^\circ)$ . Assume that the density of the  $\text{HCl}(aq)$  is  $1.0 \text{ g/mL}$ .

- (c) Calculate the magnitude of  $q$ , the thermal energy change, when the MgO was added to the  $1.0 \text{ M HCl}(aq)$ . Include units with your answer.
- (d) Determine the student's experimental value of  $\Delta H^\circ$  for the reaction between MgO and HCl in units of  $\text{kJ/mol}_{rxn}$ .
- (e) Enthalpies of formation for substances involved in the reaction are shown in the table below. Using the information in the table, determine the accepted value of  $\Delta H^\circ$  for the reaction between  $\text{MgO}(s)$  and  $\text{HCl}(aq)$ .

Substance	$\Delta H_f^\circ$ (kJ/mol)
MgO(s)	-602
H <sub>2</sub> O(l)	-286
H <sup>+</sup> (aq)	0
Mg <sup>2+</sup> (aq)	-467

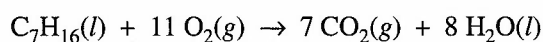
- (f) The accepted value and the experimental value do not agree. If the calorimeter leaked heat energy to the environment, would it help account for the discrepancy between the values? Explain.

2003 AP<sup>®</sup> CHEMISTRY FREE-RESPONSE QUESTIONS (Form B)

3. In an experiment, a sample of an unknown, pure gaseous hydrocarbon was analyzed. Results showed that the sample contained 6.000 g of carbon and 1.344 g of hydrogen.

- (a) Determine the empirical formula of the hydrocarbon.
- (b) The density of the hydrocarbon at 25°C and 1.09 atm is 1.96 g L<sup>-1</sup>.
  - (i) Calculate the molar mass of the hydrocarbon.
  - (ii) Determine the molecular formula of the hydrocarbon.

In another experiment, liquid heptane, C<sub>7</sub>H<sub>16</sub>(l), is completely combusted to produce CO<sub>2</sub>(g) and H<sub>2</sub>O(l), as represented by the following equation.



The heat of combustion,  $\Delta H_{\text{comb}}^\circ$ , for one mole of C<sub>7</sub>H<sub>16</sub>(l) is  $-4.85 \times 10^3$  kJ.

(c) Using the information in the table below, calculate the value of  $\Delta H_f^\circ$  for C<sub>7</sub>H<sub>16</sub>(l) in kJ mol<sup>-1</sup>.

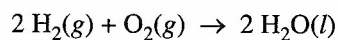
Compound	$\Delta H_f^\circ$ (kJ mol <sup>-1</sup> )
CO <sub>2</sub> (g)	-393.5
H <sub>2</sub> O(l)	-285.8

- (d) A 0.0108 mol sample of C<sub>7</sub>H<sub>16</sub>(l) is combusted in a bomb calorimeter.
  - (i) Calculate the amount of heat released to the calorimeter.
  - (ii) Given that the total heat capacity of the calorimeter is 9.273 kJ °C<sup>-1</sup>, calculate the temperature change of the calorimeter.

**2011 AP<sup>®</sup> CHEMISTRY FREE-RESPONSE QUESTIONS**

\*modified to make short response

3. Hydrogen gas burns in air according to the equation below.



- (a) Calculate the standard enthalpy change,  $\Delta H_{298}^\circ$ , for the reaction represented by the equation above.  
(The molar enthalpy of formation,  $\Delta H_f^\circ$ , for  $\text{H}_2\text{O}(l)$  is  $-285.8 \text{ kJ mol}^{-1}$  at 298 K.)
- (b) Calculate the amount of heat, in kJ, that is released when 10.0 g of  $\text{H}_2(g)$  is burned in air.
- (c) Given that the molar enthalpy of vaporization,  $\Delta H_{vap}^\circ$ , for  $\text{H}_2\text{O}(l)$  is  $44.0 \text{ kJ mol}^{-1}$  at 298 K, what is the standard enthalpy change,  $\Delta H_{298}^\circ$ , for the reaction  $2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(g)$  ?