AP Chemistry Chapter 4

Thermochemistry

Temperature

• Temperature is the measure of the average kinetic energy.



Lower average kinetic energy Lower <u>absolute</u> temperature Higher average kinetic energy Higher <u>absolute</u> temperature

Temperature

- Absolute temperature (temperature measured in Kelvin) is proportional to average kinetic energy.
- When the average kinetic energy of the particles in a sample doubles the Kelvin temperature doubles, etc.

Heat vs. Temperature

- When objects that are at different temperatures come into contact they transfer thermal energy in the form of heat.
- Heat is the flow of thermal energy from a
 - COOL HOT

Wa

Heat vs. Temperature

 The transfer of energy through heat is a result of the work done by colliding molecules on other molecules that they are in thermal contact with.



Thermal Equilibrium

 The law of conservation of energy tells us that energy is neither lost or gained. However it can be transferred.



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Thermal Equilibrium

Thin barrier Heat transfer Fast Slow between objects (end when they Elastic collision reach the same temperature and are said to be at Loses energy Gains energy thermal equilibrium. Energy transfer

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Heat Misconception

- Heat is not a substance therefore it does not make sense to say that a substance has a certain amount of heat.
- It is better stated to say that a substance contains a certain amount of thermal energy. And that "heat transfer" occurs from warmer objects to a cooler objects until thermal equilibrium is reached.

Measuring Heat and Temperature

- Temperature is measured in °C °F or K using a thermometer.
- Heat is measured in joules or calories using a calorimeter.
- 1cal. = 4.184J

Specific Heat

- Different substances require different amounts of heat to change their temperature.
- In general the specific heat of a substance indicates how hard something is to heat up or cool down.
- Scientifically speaking the specific heat is the amount of heat required to change the temperature of 1 gram of a substance by 1°C.

Substance	Specific Heat J/(g · C°)	Substance	Specific Heat J/(g · C°)
Water (liquid)	4.184	Carbon, graphite	0.720
Volumer (ice)	2.092	Carbon, diamond	0.502
View (steam)	2.013	Iron	0.444
Ethyl alcohol	2.452	Copper	0.385
Acetic acid	2.048	Silver	0.237
Sugar	1.250	Mercury	0.139
Aluminum	0.899	Gold	0.129
Salt (sodium chloride) 0.860 -	Lead	0.158

Which substance is the easiest to heat up or cool down? You may see specific heat written as 0.129 Jg^{-1°}C⁻¹

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Water (liquid)	4.184	Carbon, graphite	0.720
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A student measures out equal mass samples of aluminum, copper and silver. He adds 1000 J of energy to each sample. Explain any difference in the samples after the transfer of energy?

$q = m \Delta T C_p$

Heat = (mass) x (change in temperature) x (specific heat)

	Specific Heat	Substance	Specific Heat $V(q \cdot C^{\circ})$
Substance	J/(g·C)	Substance	sing c7
Water (liquid)	4.184	Carbon, graphite	0.720
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Aluminum	0.899	Gold	0.129
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How much heat is necessary to heat 27.8g of water from 25.0°C to 100.0°C?

8720J

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Water (liquid)	4.184	Carbon, graphite	0.720
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What is the final temperature of a 1058g copper pan at 18.0°C if 4225J of heat is added to it?

How much water do I have?



 The mass of an unknown metal is 14.9 g. It is heated to 100.0°C and dropped into 75.0 mL of water at 20.0°C. The final temperature of the system is 28.5°C. What is the specific heat of the metal? The mass of unknown metal is 17.19 g. It is heated to 100.00°C and dropped into 25.00 mL of water at 24.50°C. The final temperature of the system is 30.05°C. What is the specific heat of the metal?

0.483 Jg⁻¹°C⁻¹

Heat and Chemical Reactions

- Chemical reactions either release or absorb energy as a result of changes in bonding.
- We identify these reactions as either exothermic or endothermic.

Exothermic and Endothermic

 How do we determine whether a reaction is exothermic or endothermic?



Exothermic and Endothermic

• We measure the temperature change that occurs during the reaction.



Endothermic

- Endothermic reactions cause the surroundings to cool down.
- This is because thermal energy flows from the surroundings into the reaction.



Exothermic

- Exothermic reactions cause the surroundings to heat up.
- This is because thermal energy flows from the reaction into the surroundings.
- Exothermic reactions can also give off energy as light.



Potential Energy Diagrams

 A potential energy diagram (sometimes called simply an energy diagram), plots the change in potential energy that occurs during a chemical reaction.









Activation Energy

- Activation energy is the minimum amount of energy necessary for a reaction to occur.
- It is often illustrated on an energy diagram.

Energy for Exothermic Reaction



Energy for Endothermic Reaction



Activation Energy Video

EXOTHERMIC	ENDOTHERMIC
release energy	absorb energy
products are lower in energy than the reactants	products are higher in energy than the reactants
$-\Delta H$	$+\Delta H$
generally cause surroundings to heat up	generally cause the surroundings to cool down
nature favors these reactions	nature opposes these reactions

We say that exothermic reactions are "Thermodynamically favored".

Enthalpy (Heat) of a Change

• The heat lost or gained during the change.

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- The heat lost or gained during the change.
- **ΔH**

Calorimetry

- Calorimetry is an experimental technique that is used to measure the change in energy of a chemical system.
- We measure this heat using a calorimeter.
Calorimeter



 A chemical system is put in thermal contact with a heat bath. The heat bath is a substance, such as water, whose specific heat capacity has been well established by previous experiments. A process is initiated in the calorimeter (heating/cooling, phase transition, or chemical reaction), and the change in temperature of the water bath is measured.



 Because the specific heat of the water bath is known, the observed change in temperature can be used to determine the amount of energy exchanged between the system and the water bath.

$$\Delta T - \frac{q_{cal}}{water} system$$

Π

• $q = m \Delta T C_p$

 The energy exchanged between the system and the water bath is equal in magnitude to the change in energy of the system. If the water bath increased in temperature, the reaction is exothermic. If the water bath decreased in temperature, and therefore energy, the reaction is endothermic.



- Calorimetry can be used to measure the heat (enthalpy) associated with many types of changes.
- We will see how heats (enthalpies) of vaporization, fusion, formation, and reactions are very useful in understanding thermodynamics.





coffe-cup calorimeter

Enthalpy (Heat of Solution)

- The energy change associated with the formation of a solution.
- $\Delta H_{solution}$









The Enthalpy (Heat) of Solution ($\Delta H_{solution}$) is the sum of the enthalpy changes of these three steps



- Bonds are energy.
- Each different type of bond as an amount of energy associated with it.



- Breaking a bond requires energy to overcome the attractive forces between valence electrons and the nuclei of the atoms that form the bond.
- Therefore breaking a bond requires energy (it is an endothermic process).
- Obviously forming a bond is the opposite process and therefore releases energy (it is an exothermic process).

- All changes involve both the breaking and formation of bonds.
- The sum of the bond breakage and bond formation give us the net energy change for the reaction and determines whether the reaction is endothermic or exothermic.

- When we break a bond the process requires energy (it is endothermic).
- When we form a bond the process releases energy (it is exothermic).
- The net energy change determines whether the reaction is endothermic or exothermic.

Chemical Potential Energy

- A chemical bond can be thought of as an attractive force between atoms.
- Because of this, atoms and molecules can have chemical potential energy.
- Anytime two atoms form a strong covalent or ionic bond or two molecules form a weak van der Waals bond, chemical potential energy is converted into other forms of energy, usually heat and/or light.

Chemical Potential Energy

 The amount of energy in a bond is somewhat counterintuitive - the stronger or more stable the bond, the less chemical energy there is between the bonded atoms.

Strong bonds have low chemical energy and weak bonds have high chemical energy.

Chemical Potential Energy

- Lot's of heat and/or light energy is released when very strong bonds form, because much of the chemical energy is converted to heat and/or light energy.
- The reverse is true for breaking chemical bonds. It takes more energy to break a strong bond than a weak bond.
- The breaking of a bond requires the absorption of heat and/or light energy which is converted into chemical potential energy when the bond is broken.

A chemical reaction converts chemical energy into heat and light energy



A chemical reaction converts chemical energy into heat and light energy





Calculate the heat of solution when 1.00g of a KCIO₃ is dissolved in 50.00mL of water if the temperature of the solution falls from 25.00°C to 24.39°C? (C_p of solution = 4.18J/g•°C).

Calorimetry Lab

- Write your lab summary (purpose and procedure) (due – day after tomorrow).
- Do the Advance Study Assignment at the end of the lab (due – tomorrow).
- Use notebook paper for the assignment.
- Reading the pre-lab discussion should help you in answering some questions.

Enthalpy (Heat) of a Change

- The heat lost or gained during the change.
- **ΔH**
- Enthalpy (Heat) of combustion ∆H (See Table 4.1).
- Heat of combustion is just a specific type of heat of reaction (ΔH_{rxn}).

able 4.1

Under Standard State Conditions

Substance	Combustion Reaction	Enthalpy of Combustion, ΔH_{298}° (kJ mol ⁻¹)
Carbon	$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$	-111
	$C(s) + O_2(g) \longrightarrow CO_2(g)$	-394
Hydrogen	$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$	-242
	$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$	-286
Magnesium	$Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s)$	-602
Sulfur	$S(s) + O_2(g) \longrightarrow SO_2(g)$	-297
Carbon monoxide	$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$	-283
Methane	$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$	-802
Acetylene	$C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(g)$	-1256
Methanol	$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$	-638
sooctane	$C_8H_{18}(l) + \frac{25}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(g)$	-5460

How much heat would be released if 1.00L of isooctane (density = 0.692 g/mL) were burned?

33,100 kJ released

Enthalpy (Heat) of a Change

- The heat lost or gained during the change.
- **ΔH**
- Enthalpy (Heat) of combustion ΔH
- Enthalpy (Heat) of fusion ΔH_{fus}
- Enthalpy (Heat) of vaporization ΔH_{vap}
- Enthalpy (Heat) of formation ΔH_f

• In chemistry fusion refers to melting a solid to form a liquid.

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- The heat of fusion of ice at 0°C is 6.01 kJ/mol.
 What does this value indicate?

- In chemistry fusion refers to melting a solid to form a liquid.
- Enthalpy of fusion or heat of fusion (∆H_{fus}) refers to the amount of heat required to melt a substance.
- The heat of fusion of ice at 0°C is 6.01 kJ/mol.
 What does this value indicate?
- Write the equation for this reaction.

- In chemistry fusion refers to melting a solid to form a liquid.
- Enthalpy of fusion or heat of fusion (∆H_{fus}) refers to the amount of heat required to melt a substance.
- What is the ∆H when one mole of water freezes?

Endothermic & Exothermic

- Melting (fusion) is an endothermic process
- Freezing is an exothermic process

Temperature and State Change

- What do the values below indicate?
- $H_2O_{(s)} \rightarrow H_2O_{(l)} \Delta H = 6.01 \text{ kJ/mol}$
- $H_2O_{(I)} \rightarrow H_2O_{(s)} \Delta H = -6.01 \text{ kJ/mol}$

Temperature and State Change

- What do the values below indicate?
- $H_2O_{(s)} \rightarrow H_2O_{(l)} \Delta H = 6.01 \text{ kJ/mol}$
- $H_2O_{(I)} \rightarrow H_2O_{(s)} \Delta H = -6.01 \text{ kJ/mol}$
- Answer: Energy must be released or absorbed during a change of state.




Enthalpy (Heat) of Vaporization

• $\Delta H_{vap} = 44.01 \text{ kJ/mol} (at 25^{\circ}C).$

Enthalpy (Heat) of Vaporization

- $\Delta H_{vap} = 44.01 \text{ kJ/mol} (at 25^{\circ}C).$
- What does this value indicate?

Enthalpy (Heat) of Vaporization

- $\Delta H_{vap} = 44.01 \text{ kJ/mol} (at 25^{\circ}C).$
- What does this value indicate?
- Answer: It takes 44.01 kJ to evaporate 1 mole of water at 25°C.
- $H_2O_{(I)} \rightarrow H_2O_{(g)}$ $\Delta H_{vap} = 44.01 \text{ kJ/mol} (25^{\circ}C)$

Vaporization vs. Condensation

- $H_2O_{(I)} \rightarrow H_2O_{(g)}$ $\Delta H_{vap} = 44.01 \text{ kJ/mol} (25^{\circ}C)$
- What else can we determine from this reaction?

Vaporization vs. Condensation

- $H_2O_{(I)} \rightarrow H_2O_{(g)}$ $\Delta H_{vap} = 44.01 \text{ kJ/mol} (25^{\circ}C)$
- Would it be correct to say that it takes
 44.01 kJ to boil one mole (18.0g) of water?

Vaporization vs. Condensation

- $H_2O_{(I)} \rightarrow H_2O_{(g)}$ $\Delta H_{vap} = 44.01 \text{ kJ/mol} (25^{\circ}C)$
- Would it be correct to say that it takes
 44.01 kJ to boil one mole (18.0g) of water?
- $H_2O_{(I)} \rightarrow H_2O_{(g)}$ $\Delta H_{vap} = 40.67 \text{ kJ/mol} (100^{\circ}\text{C})$

What would we need to know to determine the total amount of heat absorbed during this process?



TABLE 2-6 SPECIFIC HEATS OF SOME COMMON SUBSTANCES						
Substance	Specific Heat J/(g · C°)	Substance	Specific Heat J/(g · C°)			
Water (liquid)	4.184	Carbon, graphite	0.720			
Valencer (ice)	2.092	Carbon, diamond	0.502			
Viterior (steam)	2.013	Iron	0.444			
Ethyl alcohol	2.452	Copper	0.385			
Acetic acid	2.048	Silver	0.237			
Sugar	1.250	Mercury	0.139			
Aluminum	0.899	Gold	0.129			
Salt (sodium chloride)	0.860	Lead	0.158			

Heat of Fusion

- What do the values below indicate?
- $H_2O_{(s)} \rightarrow H_2O_{(l)} \Delta H = 6.01 \text{ kJ/mol}$

Heating Curve for H₂O



One day while you are outside working you have 2.2 L of sweat (water) evaporate from your body. If the temperature averaged out to 25°C during the day how much excess heat did your body lose as a result of sweat evaporation?

5400 kJ

Formation Reaction

 A formation reaction is a combination reaction in which one mole of a substance is formed from free elements in their most standard states.

Enthalpy (Heat) of Formation

- The ΔH for a formation reaction.
- These are the most useful of the enthalpy changes and are designated ΔH_{f}

Write the formation reaction for $NO_2(g)$ and the corresponding ΔH . $\frac{1}{2}N_2 + O_2 \rightarrow NO_2 \Delta H = 33.2 \text{ kJ/mol}$

able 4.2	Standard Molar Enthalpies of Formation ^a		
age 113 Substance	$\frac{\Delta H_{\rm f}^{\circ}}{\rm (kJ\ mol^{-1})}$		
Carbon			
C(s, graphite)	0		
C(g)	716.68		
CO(g)	-111		
$CO_2(g)$	-394		
$CH_4(g)$	-74.8		
$CH_3OH(l)$	-238.7		
$CH_3OH(g)$	-200.7		
Chlorine			
$\operatorname{Cl}_2(g)$	0		
Cl(g)	121.7		
Hydrogen			
$H_2(g)$	0		
$H_2O(g)$	-241.8		
$H_2O(l)$	-285.83		
HCl(g)	-92.31		
$H_2S(g)$	-20.6		
Nitrogen			
$N_2(g)$	0		
NO(g)	90.25		
$NO_2(g)$	33.2		
$NH_3(g)$	-46.11		
Oxygen			
$O_2(g)$	0		
Phosphorus			
P(s)	0		
$P_4O_{10}(s)$	-2984		
$H_3PO_4(l)$	-1267		

^aSee Appendix I for additional values.

• Write the formation reaction for $CO_{(g)}$ and the corresponding ΔH .

 $C + \frac{1}{2}O_2 \rightarrow CO$ $\Delta H = -110.52 \text{ kJ/mol}$

able 4.1	Enthalpy of Combustion for One Mole of a Substance Under Standard State Conditions		Table 4.2	Standard Molar Enthalpies of Formation ^a
		Enthalpy of Combustion,	Substance	$\Delta H_{\rm f}^{\circ}$ (kJ mol ⁻¹)
Substance	Combustion Reaction	ΔH°_{298} (kJ mol ⁻¹)	Carbon	
Carbon	$C(z) \pm \frac{1}{2}O(z) \rightarrow CO(z)$		C(s, graphite)	0 716.68
Carbon	$C(s) + Q_2(g) \longrightarrow CO_2(g)$	-304	C(g)	-111
Undrogen	$C(3) + O_2(g) \longrightarrow CO_2(g)$ $H_1(g) + \frac{1}{2}O_1(g) \longrightarrow H_2O(g)$	-242	CO(g)	-394
nyulogen	$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$ $H_1(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$	-286	$CU_2(g)$ $CH_2(g)$	-74.8
Magnasium	$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $M_2(g) + \frac{1}{2}O_2(g) \longrightarrow M_2O(g)$	-200	$CH_{2}OH(l)$	-238.7
	$\operatorname{Mg}(s) + \frac{1}{2}O_2(g) \longrightarrow \operatorname{MgO}(s)$	-002	$CH_3OH(g)$	-200.7
Sullul	$S(3) + O_2(g) \longrightarrow SO_2(g)$ $CO(g) + \frac{1}{2}O(g) \longrightarrow CO(g)$	-297		
Vathana	$CU(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$ $CU(g) + 2O(g) \longrightarrow CO_2(g)$	-203	Chlorine	0
Acatulana	$C H_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$ $C H_4(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O_2(g)$	-1256	$Cl_2(g)$	121.7
Mathanal	$C_{2}\Pi_{2}(g) + {}_{2}O_{2}(g) \longrightarrow 2CO_{2}(g) + \Pi_{2}O(g)$ $C_{2}\Pi_{2}(g) + {}_{2}O_{2}(g) \longrightarrow 2CO_{2}(g) + \Pi_{2}O(g)$	-638	CI(g)	121.7
	$C \stackrel{\text{H}}{\to} (l) + \frac{25}{2} O_2(g) \longrightarrow CO_2(g) + 2\Pi_2O(g)$	-5160	Hydrogen	
isooctane	$C_8H_{18}(l) + \frac{1}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(g)$	- 3400	$H_2(g)$	0
			$H_2O(g)$	-241.8
			$H_2O(l)$	-285.83
			HCl(g)	-92.31
Comr	hare ΛH values for	r CO	$H_2S(g)$	-20.6
Comp	are Arr values in		Nitrogen	
			$N_2(g)$	0
			NO(g)	90.25
			$NO_2(g)$	33.2
			$NH_3(g)$	-46.11
			Ovygen	
			$O_{\mathbf{x}}(q)$	0
			02(8)	
			Phosphorus	A series of the second s
			P(<i>s</i>)	0
			$P_4O_{10}(s)$	-2984
			$H_3PO_4(l)$	-1267

^aSee Appendix I for additional values.

• Write the formation reaction for $CH_3OH_{(g)}$ and the corresponding ΔH .

 $C + 2H_2 + \frac{1}{2}O_2 \rightarrow CH_3OH$ $\Delta H = -200.7 \text{ kJ/mol}$

• Write the formation reaction for $H_3PO_{4(I)}$ and the corresponding ΔH .

 $3/2 H_2 + P + 2O_2 \rightarrow H_3PO_4$ $\Delta H = -1267 \text{ kJ/mol}$

• Write the formation reaction for $Cl_{(g)}$ and the corresponding ΔH . $\frac{1}{2}Cl_{2} \rightarrow Cl$ $\Delta H = +121.68 \text{ kJ/mol}$

• Write the formation reaction for $Cl_{2(g)}$ and the corresponding ΔH .

 $Cl_2(g) \rightarrow Cl_2(g)$ $\Delta H = 0 kJ/mol$

No Reaction

Review Section of Chapter 4 Test

 Analysis of Lab Data (Determination of an Empirical Formula).

Hess's Law

Fe + 3/2Cl₂ → FeCl₃ \triangle H = ? = -399.5 kJ • Use the information below to determine the \triangle H for the reaction. Fe + Cl₂ → FeCl₂ \triangle H = -341.8 kJ FeCl₃ → FeCl₂ + ¹/₂ Cl₂ \triangle H = +57.7 kJ $\begin{array}{l} \mathsf{P}_4\mathsf{O}_{10}+\mathsf{6H}_2\mathsf{O}_{(\mathsf{I})}\to \mathsf{4H}_3\mathsf{PO}_4\ \ \Delta\mathsf{H}=?\\\\ \text{Use the information below to determine the } \Delta\mathsf{H}.\\\\ \mathsf{4P}+\mathsf{5O}_2\to\mathsf{P}_4\mathsf{O}_{10}\ \ \Delta\mathsf{H}=-\mathsf{2984}\ \mathsf{kJ}\\\\ \mathsf{H}_2+\frac{1}{2}\ \mathsf{O}_2\to\mathsf{H}_2\mathsf{O}_{(\mathsf{I})}\ \ \Delta\mathsf{H}=-\mathsf{285}.\mathsf{83}\ \mathsf{kJ}\\\\ \mathsf{3/2}\ \mathsf{H}_2+\mathsf{P}+\mathsf{2O}_2\to\mathsf{H}_3\mathsf{PO}_4\ \ \Delta\mathsf{H}=-\mathsf{1267kJ} \end{array}$



$\Delta H = \sum \Delta H_{f(products)} - \sum \Delta H_{f(reactants)}$ $P_4O_{10} + 6H_2O_{(I)} \rightarrow 4H_3PO_4 \quad \Delta H = -369 \text{ kJ}$

$$\Delta H = \sum \Delta H_{f(products)} - \sum \Delta H_{f(reactants)}$$

Determine $\triangle H$ for the reaction using the above formula. $4NH_{3(g)} + 7O_{2(g)} \rightarrow 4NO_{2(g)} + 6H_2O_{(I)}$



 $\Delta H = \sum \Delta H_{f(products)} - \sum \Delta H_{f(reactants)}$

Determine $\triangle H$ for the reaction using the above formula. $2AI_{(s)} + Fe_2O_{3(s)} \rightarrow AI_2O_{3(s)} + 2Fe_{(s)}$



 $\Delta H = \sum \Delta H_{f(products)} - \sum \Delta H_{f(reactants)}$

Determine $\triangle H$ for the reaction using the above formula. $2NH_{3(g)} + 3O_{2(g)} + 2CH_{4(g)} \rightarrow 2HCN_{(g)} + 6H_2O_{(g)}$

