CHE 1031: General Chemistry I



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8. Thermochemistry

- 8.1: Energy basics
- 8.2: Calorimetry
- 8.3: Enthalpy

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8. Thermochemistry

8.1: Energy basics

- Define energy, distinguish between types of energy, and describe the nature of energy changes that accompany physical and chemical changes.
- Distinguish between heat, thermal energy & temperature.
- Define and distinguish specific heat and heat capacity and describe the physical implications of both.
- Perform calculations involving heat, specific heat and changes in temperature.

Chemical changes ~ energy changes



Many, if not most, of the chemical changes we observe and use daily involve **changes in energy**:

- Cooking food to make nutrients more bioavailable;
- Burning fuels to provide heat, motive power and electricity; &
- Chemical processing of raw materials to create materials for use to use.

More than 90% of our energy comes from the sun, though it may flow to us through physical changes (wind) and chemical changes (photosynthesis).



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Energy



Energy: the capacity to supply heat (q) or do work (w)

- Moving objects in opposition to forces like friction & gravity
- **Potential energy:** the energy an object possesses by virtue of its position; <u>stored energy</u>
 - Chemical energy is potential energy. (batteries, fuels)

Kinetic energy: the energy of objects in motion





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First law of thermodynamics



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First law of thermodynamics: energy is conserved, neither created nor destroyed, but only transferred or transformed

Transfer? From one object to another

· Heat always flows from hot objects to cooler objects

Transformed? From one form to another

- Kinetic energy can become potential energy (or vv).
- Potential or kinetic energy can become heat.

You push a watermelon off out of a third-floor window. How is energy transferred or transformed?



Thermal energy

Thermal energy: kinetic energy of the random motion of atoms and molecules

Temperature: quantitative measure of 'hot' and 'cold'

• Faster kinetic motion (sometimes called vibration) results in more thermal energy and a higher temperature.



Hot water





Heat (q) (heat flow): the transfer of thermal energy between two bodies at different temperatures: from hot to cold.

• Heat flow continues until both bodies are the <u>same</u> <u>temperature</u>.



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Endo- vs. exothermic reactions



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Endothermic: processes that <u>require</u> an input of energy or heat in order to occur.

• ∆H = +

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• Example: dehydration of a hydrated salt

Exothermic: processes that <u>release</u> energy or heat as they occur.

- ΔH = -
- Example: combustion of gasoline



Units & heat capacity

Joule (J): the amount of energy used when a force of 1 Newton is used to move an object 1 meter

- $1 J = 1 \text{ kg m}^2/\text{s}^2$
- 1 kJ = 1000 J

Heat capacity: the amount of energy needed to raise an object's temperature by 1 degree C

c = <u>q</u> = <u>J</u> ΔT °C

Calculate the heat capacity of two cast-iron frying pans, one large and one small. The temperature of each pan is increased by 50 degrees. That requires an input of 18,150 J of energy for the small pan, and 90,700 J for the large pan.

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Specific heat



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Specific heat: the amount of energy used to raise the temperature of 1 g of substance by $1 \degree C$

- Unit: J/g-°C
- Water = 4.184 J/g-°C

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$$= \frac{q}{(m)(\Delta T)} = \frac{J}{g^{-} c}$$

Calculate the specific heat of two cast-iron frying pans, one large and one small. The temperature of each pan is increased by 50 degrees. That requires an input of 18,150 J of energy for the small pan, and 90,700 J for the large pan. The mass of the small pan is 808 g and the large pan is 4040 g.

Common specific heat values

Specific Heats of Common Substances at 25 °C and 1 bar

Substance	Symbol (state)	Specific Heat (J/g	°C)			
helium	He(g)	5.193				
water	H ₂ O(<i>l</i>)	4.184				
ethanol	C2H6O(/)	2.376				
ice	H ₂ O(s)	2.093 (at −10 °C))			
water vapor	H ₂ O(g)	1.864	Speci	fic Heats d	of Common Subst	ances at 25 °C and 1
nitrogen	Nb(g)	1.040			Original (second)	0

Substance	Symbol (state)	Specific Heat (J/g °C)
air		1.007
oxygen	O ₂ (g)	0.918
aluminum	Al(s)	0.897
carbon dioxide	CO ₂ (g)	0.853
argon	Ar(g)	0.522
iron	Fe(s)	0.449
copper	Cu(s)	0.385
lead	Pb(s)	0.130
gold	Au(s)	0.129
silicon	Si(s)	0.712

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Calculating change of heat

If we know the mass of a substance, its specific heat and the change in temperature, we can calculate the heat flow using:

 $q = (c)(m)(\Delta T)$ units: J = (J/g-°C)(g)(°C)

 $q = \Delta H$ + ΔH = endothermic - ΔH = exothermic

A flask containing 8.0 E2 g of water is heated and the temperature of the water increases from 21 to 85° C. How much heat was used?

Calculating other parameters



A piece of metal has a mass of 348 g and absorbs 6.64 kJ of heat as its temperature increases from 22.4 to 43.6° C. Calculate the specific heat of the metal, and try to identify it.

A piece of metal weighs 217 g and absorbs 1.43 kJ of heat. Its temperature increases from 24.5 to 39.1°C. Calculate the metal's specific heat.

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Using molten salt to store energy

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A solar power plant stores energy overnight by melting salt: a mixture of sodium nitrate and potassium nitrate. If one ton of this salt, with a heat capacity of 1.53 J/g- $^{\circ}$ C, is heated from 260 to 550 $^{\circ}$ C, how much energy can be stored?

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Can you?

- (1) Define the term 'energy' and differentiate between potential, kinetic and chemical energy?
- (2) State the first law of thermodynamics?
- (3) Explain the relationship between thermal energy and heat? What do thermometers measure?
- (4) Define, and differentiate between, processes that are endothermic and exothermic?
- (5) Define (and know the units for) heat capacity and specific heat?
- (6) Use specific heat, mass and change in temperature to calculate heat changes?

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8. Thermochemistry

8.2: Calorimetry

- Explain the technique of calorimetry
- Calculate and interpret heat and related properties using typical calorimetry data



This **'adiabatic' insulated** calorimeter uses <u>indirect</u> <u>measurement</u> of the system: it measures temperature changes in the surroundings. Thus, $q_{system} = (-) q_{surroundings} = (-)(c)(m)(\Delta T)$



exothermic

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Calorimetry calculations

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A 360-g piece of steel rebar is dropped into 425 mL of water at 24°C. Water temperature increased to 42.7°C. The specific heat of iron is 0.449 J/g-°C. What was the initial temperature of the rebar?

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Try this

A 59.7-g piece of metal was submerged in boiling water and then quickly transferred into 60.0 mL of water whose Initial temperature was 22.0C. The final temperature is 28.5C. What is the specific heat of the metal? Its identity?

Try this When 50.0 mL of 1.00 M HCl and 50.0 mL of 1.00 M NaOH, 10 both at initial temperatures of 22.0C, are mixed in a calorimeter, the temperature of the solution increases to 28.9C.

How much heat is produced by the reaction?

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And this

When 3.00 g of KCl is added to 3.00 E2 g of water in a calorimeter, the temperature decreased by 1.05° C. How much heat is involved in dissolution of KCl? \bigcirc

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Can you?



- (1) Explain the purpose of calorimetry?
- (2) Explain the difference between open and closed systems?
- (3) Explain how the terms system and surroundings apply to chemistry?
- (4) Explain why the heat change (Δ H) of the system is the negative Δ H of the calorimeter?
- (5) Use the relationships between mass, specific heat, change in temperature and heat change to solve for one variable if given the others.

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8. Thermochemistry

8.3: Enthalpy

- State the first law of thermodynamics
- Define enthalpy and explain its classification as a state function.
- Write and balance thermochemical equations.
- Calculate enthalpy changes for chemical reactions.
- Explain Hess's law and use it to calculate enthalpies of reactions.

Internal energy (U)

Internal energy (U): the sum of all types of energy in a system

 $\Delta U = q + w$ where q is heat & w is work

- + **q**, + **w** mean that heat & work are being transferred from the surroundings into the system.
- - **q**, **w** mean that heat & work are being transferred from the system into the surroundings.



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Enthalpy change (ΔH)

For processes that occur at constant pressure and that don't involve change of pressure and volume, **enthalpy** is the heat flow resulting from the chemical reaction.

qp =∆H

Thermochemical equations: balanced chemical equations that include heat flows as ΔH .

 $H_2(g) + 1/2O_2(g) \rightarrow H_2O(I)$ $\Delta H = -286 \text{ kJ} \text{ (exothermic)}$

Rules for using thermochemical equations:

- (1) ΔH is extensive: the amount of energy varies with mass.
- (2) ΔH depends on physical state.
- (3) When the direction of a reaction is reversed, the sign of ΔH is changed.



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	H2(g) + 1/2O2(g) → H2O(l)	ΔH = -286 kJ	
(1)	2H2(g) + O2(g) → 2H2O(l) ½H2(g) + ¼O2(g) → ½H2O(l)	ΔH = (2)(-286 kJ) ΔH = -286 kJ/2	extensive
(2)) H2(g) + 1/2O2(g) → H2O(g)	ΔH = -242 kJ	physical state
(3) H2O(I) → H2(g) + 1/2O2(g)	ΔH = +286 kJ	reversible

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Thermochemical equations: distributive

 $H_2(g) + 1/2O_2(g) → H_2O(I)$ ΔH = -286 kJ

The **distributive property** of thermochemical equations allows us to make conversion factors from them.

<u>1 mole H2</u>	<u>½ mole O2</u>	<u>1 mole H2O</u>	And each can
- 286 kJ	- 286 kJ	- 286 kJ	be flipped.

How much energy is produced when 28.5 g of water are made?

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Hess's law

Hess's law: if a process can be broken into several steps, the ΔH of the whole process is equal to the sum of ΔH values for each step.

 Allow's calculation of enthalpy changes of complex reactions from databases of simpler reactions without experimental work.

What if we want the calculate the ΔH of this combustion reaction but don't have a bomb calorimetere (needed for combustion reactions)?

 $C(s) + O2(g) \rightarrow CO2(g) \qquad \Delta H =$

We can find this information:

$$+ \frac{C(s) + 1/2O2(g) \rightarrow CO(g)}{CO(g) + 1/2O2(g) \rightarrow CO2(g)} \Delta H = -111 \text{ kJ}$$

$$\frac{CO(g) + 1/2O2(g) \rightarrow CO2(g)}{C(s) + O2(g) \rightarrow CO2(g)} \Delta H = -394 \text{ kJ}$$

Consider extensive & reversible-ness



Determine the ethalpy of formation of FeCl₃ from these equations:

Fe(s) + Cl2(g)
$$\rightarrow$$
 EeCl2(s) $\Delta H = -341.8 \text{ kJ}$ FeCl2(s) + $\frac{1}{2}$ Cl2(g) \rightarrow FeCl3(s) $\Delta H = -57.7 \text{ kJ}$

Want: $Fe(s) + 3/2Cl_2(g) \rightarrow FeCl_3(s)$ $\Delta H = -399.5 \text{ kJ}$

Look for species unique to each given equation and the equation you want.

- Are they on the same side? If not, reverse equation given.
- Are there the right number of moles? If not, fudge factor



Try this Use reactions 1-3 to calculate the enthalpy for this reaction: $CIF(g) + F2(g) \rightarrow CIF3(g)$ (1) $2OF2(g) \rightarrow O2(g) + 2F2(g)$ (2) $2CIF(g) + O2(g) \rightarrow CI2O(g) + OF2(g)$ (3) $CIF3(g) + O2(g) \rightarrow 1/2CI2O(g) + 3/2OF2(g)$ $\Delta H = +205.6$ kJ (3) $CIF3(g) + O2(g) \rightarrow 1/2CI2O(g) + 3/2OF2(g)$ $\Delta H = +266.7$ kJ

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One more	Ó
Aluminum chloride can be formed from its eleme $2AI(s) + 3CI_2(g) \rightarrow 2AICI_3(s)$	ents: 16 ΔH =
(1) HCl(g) \rightarrow HCl(aq) (2) H2(g) + Cl2(g) \rightarrow 2HCl(g) (3) AlCl3(aq) \rightarrow AlCl3(s) (4) 2Al(s) + 6HCl(aq) \rightarrow 2AlCl3(aq) + 3H2(g)	ΔH = - 74.8 kJ ΔH = - 185.0 kJ ΔH = + 323 kJ ΔH = - 1049 kJ

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Can you?

- (1) Define the term 'internal energy' and relate it to heat and work?
- (2) Define the term 'thermochemical equation' and describe its properties?
- (3) Create conversion factors from thermochemical equations and use them to solve problems?
- (4) State Hess's law and use it to calculate the enthalpies of complex chemical reactions from simpler reactions?

Key terms & equations to know



standard enthalpy of combustion (ΔHc °) bomb calorimeter calorie (cal) standard enthalpy of formation (ΔHf °) calorimeter standard state state function calorimetry surroundings chemical thermodynamics endothermic process system energy temperature enthalpy (H) thermal energy enthalpy change (ΔH) thermochemistry exothermic process work (w) expansion work (pressure-volume work) first law of thermodynamics heat (q) heat capacity (C) • $q = c \times m \times \Delta T = c \times m \times (T_{\text{fina}} - T_{\text{initial}})$ Hess's law • $\Delta U = q + w$ hydrocarbon internal energy (U) $\Delta H_{\text{reaction}}^{\circ} = \sum n \times \Delta H_{\text{f}}^{\circ} \text{ (products)} - \sum n \times \Delta H_{\text{f}}^{\circ} \text{ (reactants)}$ joule (J) kinetic energy nutritional calorie (Calorie) potential energy specific heat capacity (c in J/g-C)

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