

CHEMICAL REACTIVITY

What drives chemical reactions? How do they occur, and how fast?

The first question is answered by

THERMODYNAMICS, and the second question is answered by **KINETICS**.



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CHEMICAL REACTIVITY

THERMODYNAMICS dictates if the reaction will occur or not.



Paper will combine with oxygen to burn





CHEMICAL REACTIVITY

KINETICS dictates how fast the reaction will occur.

Example: diamond into graphite is thermodynamically favored, but the kinetics of the reaction is too slow to be of useful





CHEMICAL REACTIVITY

We have already seen a number of "driving forces" for reactions that are PRODUCT-FAVORED.

- formation of a precipitate (precipitation)
- gas formation (gas forming)
- H₂O formation (acid-base)
- electron transfer (redox) i.e. in a battery

In general, reactions that transfer energy to their surroundings are productfavored.





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Potential Energy

- Two types of energy: potential energy and kinetic energy
- Potential energy energy due to position or composition, "stored energy"

In chemistry, positive and negative particles (ions) attract one another electrostatic energy. Also: gravitational, nuclear

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NaCl - composed of Na⁺ and Cl⁻ ions.



System and Surroundings

Iso A d



The system includes the molecules we want to study (here, the hydrogen and oxygen molecules).
The surroundings are everything else (here, the

cylinder and piston; could be water, solvent, air, etc.)



		Grated cheese
ated system: termos bottle taining hot soup with lid occurrent on tightly	(b) Closed system: A cup of hot soup with a lid	(c) Open system: An open hot soup

Directionality of Heat Transfer

Heat always transfers from the hot object to the cooler object.

EXOthermic: heat transfers from SYSTEM to SURROUNDINGS.



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Directionality of Heat Transfer

Heat always transfers from the hot object to the cooler object.

ENDOthermic: heat transfers from SURROUNDINGS to the SYSTEM.

Enthalpy of Reaction

The quantity, ΔH , is called the enthalpy of

usually measured in kJ/mol

reaction (ΔH_{rxn}), or the heat of reaction and is



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T(system) goes up T(surr) goes down this is what we usually measure



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 $\Delta \mathbf{E} = \mathbf{q} + \mathbf{w}$ and $\Delta \mathbf{E} = \Delta \mathbf{H} + \mathbf{w} \quad (P \text{ const})$

Enthalpy (ΔH)

The Truth About Enthalpy

 ΔH for a reaction in the forward direction is equal in size, but opposite in sign, to ΔH for the reverse reaction.

• Enthalpy (ΔH) is heat (q) transferred at constant

• $\Delta H > 0$, Endothermic; $\Delta H < 0$, Exothermic • Add subscripts to indicate ΔH for specific process

pressure (i.e. $\Delta H = q_P$)

i.e., ΔH_{vap} , ΔH_{rxn} , ΔH_{f}

 ΔH for a reaction depends on the state of the products and the state of the reactants.



We cannot know the exact enthalpy of the reactants and products, but we measure ΔH through calorimetry, the measurement of heat flow.



Bomb calorimeter

Calorimetry

 $2 H_2(g) + O_2(g)$

Calorimetry is the measure of heat (energy) transfer



Heat energy is associated with molecular motions (Kinetic Molecular Theory)

Heat transfers until thermal equilibrium is established

Heat & Matter - no change in state



When matter absorbs heat (q, in J), its temperature (ΔT) will rise depending on its mass (m, in g) and specific heat capacity (C):



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Specific Heat Capacity

The heat (J) required to raise 1 g of an object by 1 °C (or K) Memorize 4.184 for water



Aluminum



Substance $H_2O(I)$ Ethylene glycol(l) AI(s) glass(s)



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Specific Heat Capacity

A piece of iron (88.5 g) at 77.8 °C is placed in 244 g of water at 18.8 °C. What is the final temperature of the mixture?

By the law of conservation of energy:

$$\mathbf{q}_{hot} + \mathbf{q}_{cold} = \mathbf{0}, ol$$

 $m_{Fe}C_{Fe}\Delta T_{Fe} + m_{water}C_{water}\Delta T_{water} = 0$ C_{Fe} = 0.449 J g⁻¹ K⁻¹

Final Temperature (warm) same for Fe & H₂O



Fe (88.5 g, 0.449 J/g•K, 77.8 °C) and water (244 g, 4.184 J/g•K, 18.8 °C); final temperature?

$q_{hot} + q_{cold} = 0$

 $m_{Fe}C_{Fe}\Delta T_{Fe}$ + $m_{water}C_{water}\Delta T_{water}$ = 0 88.5 * 0.449 * (T_f - 77.8) + 244 * 4.184 * (T_f - 18.8) = 0 $39.7T_f - 3090 + 1020T_f - 19200 = 0$ 1060T_f = 22300

T_f = 21.0 °C

Efficient method to determine approximate final temperature of mixture

Heat Transfer No Change in State

q transferred = (mass)(sp. ht.)(ΔT)



Heat & Changes of State



When matter absorbs heat, its temperature will rise until it undergoes a *Phase Change* (solid to liquid, liquid to gas, solid to gas)

The matter will continue to absorb energy, however during the phase change its temperature remains constant (no Δ T): Phase changes are "*Isothermal*" processes.

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Standard Enthalpy Values

Most ∆H values are labeled ∆H°Measured (°) under standard
conditionsP = 1 bar (approx. 1 atm)
Concentration = 1 mol/L
T = usually 25 °Cwith all species in standard states

with all species in standard state i.e., $C = graphite and O_2 = gas$



∆ = change in H = heat energy

0 = standard conditions

 \mathbf{x} = type of change

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Thermochemical Equations

Thermochemical equations are regular chemical equations with an energy term.

 $\mathrm{CH}_4(g) + 2 \mathrm{O}_2(g) \rightarrow \mathrm{CO}_2(g) + 2 \mathrm{H}_2\mathrm{O}(g) \qquad \Delta\mathrm{H^o} = -802 \mathrm{~kJ}$

 $CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(g) + 802 \text{ kJ}$

Energy is a **product** just like CO₂ or H₂O! (Exothermic)

This provides new conversion factors! From the equation:

 $\frac{+802 \text{ kJ of Energy Released}}{1 \text{ mol CH}_4(g) \text{ consumed}}$

 $\frac{+802 \text{ kJ of Energy Released}}{2 \text{ mol H}_2 \text{O (g) produced}}$

 $\label{eq:example:How many kJ of energy are released when 128.5 g of methane, CH_4(g), are combusted?$

$$CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(g) \Delta H^\circ = -802 \text{ kJ}$$

g → mols→ J ↑ ↑ molar Reaction mass enthalpy

$$128.5g CH_4 \times \frac{1 \text{ mol } CH_4}{16.04 \text{ g}} \times \frac{1 \text{ mol } rxn}{1 \text{ mol } CH_4} \times \frac{-802 \text{ kJ}}{1 \text{ mol } rxn} = -6.43 \times 10^3 \text{ kJ}$$

Enthalpy Values

 ΔH values depend on how the reaction is written and on phases of reactants and products

 $\begin{array}{l} H_2(g) + 1/2 \ O_2(g) \dashrightarrow H_2O(g) \\ & \Delta H^\circ_1 = -242 \ kJ \\ 2 \ H_2(g) + O_2(g) \dashrightarrow 2 \ H_2O(g) \\ & \Delta H^\circ_2 = -484 \ kJ = 2^* \ \Delta H^\circ_1 \\ H_2O(g) \dashrightarrow H_2(g) + 1/2 \ O_2(g) \\ & \Delta H^\circ_3 = +242 \ kJ = -(\Delta H^\circ_1) \\ H_2(g) + 1/2 \ O_2(g) \dashrightarrow H_2O(\text{liquid}) \\ & \Delta H^\circ_4 = -286 \ kJ \neq \ \Delta H^\circ_1 \end{array}$

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USING ENTHALPY

Making H₂O from H₂ involves two steps. <mark>H₂(g) + 1/2 O₂(g) ---> H₂O(g) + 242 kJ</mark> H₂Q(g) ---> H₂O(liq) + 44 kJ

H₂(g) + 1/2 O₂(g) --> H₂O(liq) + 286 kJ Example of HESS'S LAW-

If a rxn. is the sum of 2 or more others, the net ΔH is the sum of the ΔH 's of the other rxns.



Hess's Law Problem	Compound AH _f (kJ/mol) Compound AH _f (kJ/m	10
Example: Determine the ΔH° for the reaction: 3 H ₂ (g) + N ₂ (g) \rightarrow 2 NH ₃ (g) $\Delta H^{\circ}_3 = ???$	Standard Enthalpy Values AgBr(s) -99.5 C ₂ H ₂ (g) +226.7	
(1) $2 H_2(g) + N_2(g) \rightarrow N_2 H_4(g) \ \Delta H^\circ_1 = +95.4 \text{ kJ}$ (2) $N_2 H_4(g) + H_2(g) \rightarrow 2N H_3(g) \ \Delta H^\circ_2 = -187.6 \text{ kJ}$	NIST (Nat'l Institute for Standards and $\rm C_2H_4(g)$ +52.3 Technology) gives values of	
Desired equation has no N_2H_4 , so try to remove by adding equations (1) & (2) together:	∆H _f %gi standard molar4enthalpy of C ₂ H ₆ (g) -84.7 formation	
$2 H_2(g) + N_2(g) + N_2 H_4(g) + H_2(g) \rightarrow N_2 H_4(g) + 2NH_3(g)$	- the enthalpy change when 1 mol of C ₃ H ₈ (g) =103.8	
Combine like terms, reduce to: $3 H_2(g) + N_2(g) \rightarrow 2 NH_3(g) \Delta H_{o_3}$	compound is formed from elements under standard conditions 31.8 n-C ₄ H ₁₀ (g) -124.7	
And get: $\Delta H^{\circ}_{3} = \Delta H^{\circ}_{1} + \Delta H^{\circ}_{2} = +95.4 \text{ kJ} + (-187.6 \text{ kJ}) = -92.2 \text{ kJ}$	These values are available in your text All elements in standard states have $\Delta H_{f}^{\circ} = 0$ (graphite but $12^{(1)}$ = 173.1 not diamond, $O_2(g)$ but not O_3 or $O_2(I)$, etc.)	
	<i>MAR</i> BaCl ₂ (s) -860.1 C ₂ H ₅ OH(l) -277.6	

Question: What is the standard molar enthalpy of formation equation for potassium permanganate?

elements	compound

- $K(s) + Mn(s) + 2O_2(g) \longrightarrow KMnO_4(s)$
- · salts, metals: solids at standard state conditions. oxygen is a gas
- · balance for one mole of the product; reactants elements in their standard states



KMnO4(aq) and KMnO4(s)

Using Standard Enthalpy Values



In general, when ALL enthalpies of formation are known:

 $\Delta \mathbf{H}_{rxn} = \Sigma \mathbf{n} \Delta \mathbf{H}_{f^0} (\text{products}) - \Sigma \mathbf{n} \Delta \mathbf{H}_{f^0} (\text{reactants})$

 Σ = summation sign, or "add up all of the" n = stoichiometric coefficients "Energy gained" - "Energy spent"

Using Standard Enthalpy Values

Example: Find ΔH^{o}_{rxn} for $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ using:

$\Delta H^{o}_{rxn} = \Sigma n \Delta H_{f^{o}} (prod) - \Sigma n \Delta H_{f^{o}} (react)$

Answer: $\Delta H^{o}_{rxn} = \{ \Delta H_{f^{o}} (CaO) + \Delta H_{f^{o}} (CO_{2}) \} - \{ \Delta H_{f^{o}} (CaCO_{3}) \}$ ∆H^o_{rxn} = {-635.1 + -393.5} - {-1206.2} ∆Ho_{rxn} = +177.6 kJ All stoichiometries (n) are one in this example

Using Standard Enthalpy Values

Calculate the heat of combustion of methanol, i.e., ΔH^{o}_{rxn} for

$CH_3OH(g) + 3/2 O_2(g) --> CO_2(g) + 2 H_2O(g)$

 $\Delta H^{o}_{rxn} = \Sigma n \Delta H_{f^{o}} (prod) - \Sigma n \Delta H_{f^{o}} (react)$

As before, look up $\Delta H_{f^{o}}$ values for reactants and products in your text

Elements in standard states have $\Delta H_{f^{0}} = 0$

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Measuring Heats of Reaction: CALORIMETRY

Step 1: Calculate heat transferred from reaction to water.

q = (1200. g)(4.184 J/g·K)(8.20 K) = 41,200 J

Step 2: Calculate heat transferred from reaction to bomb

 $q = (bomb heat capacity)(\Delta T)$

= (837 J/K)(8.20 K) = 6860 J

Step 3: Calculate total heat absorbed

41,200 J + 6860 J = 48,100 J * kJ/10³ J = 48.1 kJ

Step 4: Total heat evolved = -(Total heat absorbed) = - 48.1 kJ

Heat of combustion *for 1.00 g of octane* = (-48.1 kJ / 1.00 g) * (114.23 g / mol C₈H₁₈) = -5.49*10³ kJ/mol

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octane is C₈H₁₈, 114.23 g/mol MAR



memorize 4.184 J/g°C heat capacity liquid water q = mCΔT heat transfer no change in phase q = "heat"x"mass" heat transfer with change in phase

be able to use Hess's Law

understand Heat of Formation, $\Delta H_{t^{o}}(1 \text{ mol product, reactants are elements in standard states})$

 $\label{eq:linear} \begin{array}{l} \textit{understand how to use:} \\ \Delta H^o_{rxn} = \Sigma \; n \Delta H_f^o \left(\textit{prod} \right) \textbf{-} \Sigma \; n \Delta H_f^o \left(\textit{react} \right) \end{array}$

End of **Chapter Five**

See also:

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- <u>Chapter Five Study Guide</u>
- Chapter Five Concept Guide
- · Important Equations (following this slide)
- End of Chapter Problems (following this slide)



EXOTHERMIC REACTIONS?



Important Equations, Constants, and Handouts from this Chapter:

Thermodynamics:

- endothermic & exothermic
- · product & reactant favored
- Law of Conservation of Energy
- units of energy (J, kJ, cal, etc.) system & surroundings

- formation
- · standard enthalpy conditions
- · Hess's Law

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 $\Delta H^{o}_{rxn} = \Sigma n \Delta H_{f^{o}}$ (products) - $\Sigma n \Delta H_{f^{o}}$ (reactants)

 $\Delta E = q + w = 0$

change)

q = mC∆T (no phase

("mass") (phase change)

memorize Cwater(liquid) =

4.184 J g⁻¹ K⁻¹

q = (heat of "something")

End of Chapter Problems: Test Yourself

- The initial temperature of a 344 g sample of iron is 18.2 °C. If the sample absorbs 2.25 kJ of heat, what is its final temperature? Cre = 0.449 J/g K
 One beaker contains 156 g of water at 22 °C and a second beaker contains 85.2 g of water at 95 °C. The water in the two beakers is mixed. What is the final water temperature?
 What quantity of heat is required to vaporize 125 g of benzene, CeHe, at its boiling point, 80.1 °C? The heat of vaporization of benzene is 30.8 kJ/ mol
- mol. mov. 4. The enthalpy changes for the following reactions can be measured: $CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(g)$ $AH^\circ = -802.4 \text{ kJ}$ $CH_5OH(g) + 3J 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(g)$ $AH^\circ = -876 \text{ kJ}$ Use these values and Hess's law to determine the enthalpy change for the
- reaction: $CH_4(g) + 1/2 O_2(g) \rightarrow CH_3OH(g)$ 5. Write a balanced chemical equation for the formation of Li₂CO₃(s) from the elements in their standard states. Find the value of $\Delta H_{f^{\circ}}$ for Li₂CO₃(s) in a table of values.
- Ca(OH)₂ reacts slowly with CO₂ to give CaCO₃: Ca(OH)₂(s) + CO₂(g) \rightarrow CaCO₃(s) + H₂O(g) Calculate the standard enthalpy change for this 6. reaction

End of Chapter Problems: Answers

- $\begin{array}{ll} 1. & 306.0 \text{ K} (32.8 \ ^{\text{O}}\text{C}) \\ 2. & 321 \text{ K} (48 \ ^{\text{O}}\text{C}) \\ 3. & 49.3 \text{ kJ} \\ 4. & -126 \text{ kJ} \\ 5. & 2 \text{ Li}(s) + \text{C}(s) + 3/2 \\ 6. & \Delta \text{H}^{\circ}_{\text{CM}} = -83.1 \text{ kJ} \end{array}$

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 heat & work · enthalpy calorimetry · heat of reaction and heat of