

# CHM3400 Resources

Chapter 2 & 3: The First Law of Thermodynamics FLORIDA INTERNATIONAL UNIVERSITY

### Thermochemistry

•The study of energy in chemical reactions

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- It is a sub-discipline of Thermodynamics (study of the movement of heat)
- It is the study of the **bulk** properties of matter and deduces a few general laws
  - -It does not require any knowledge or assumptions of molecules



## Thermochemistry Definitions

System - The part of the universe we chose to study

 ${\bf Surroundings}$  – The rest of the universe (normally we only worry about the immediate surroundings)

**Process** – A physical occurrence (usually involving energy flow)

 $\ensuremath{\textbf{Open System}}$  – A system where energy and matter can be exchanged with the surroundings

Closed System-A system where energy (but not matter) can be exchanged with the surroundings

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### **Thermochemistry Definitions**

### Systems and Energy

• All systems contain energy

- In thermodynamics we are interested in the flow of energy, particularly in the forms of heat and work

• The system has energy (often described as the ability to do work). It does not have heat or energy

\*Note: Heat and work only occur when there is a process. They only exist when something happens.



## Thermochemistry Definitions

### Heat

- Energy that is transferred between a system and its surroundings as a result of temperature differences
- Heat transfer can change the temperature of somethings, but does not always do (only) that.
- •Heat transfer can cause a phase change (eg melt or vaporize material).

# **EVEN** Heat • In the case of a material that does not change phase, the increase in temperature ( $\Delta T$ ) due to the input of a given amount of heat 'q' is given by: $q = c\Delta T$ • The heat capacity (c) is a constant that depends on the system, so, it's not useful. It has units J/K • It is better to be able to define the heat capacity in terms of a specific material or compound. This is defined by: $q = nC\Delta T$ , or $q = mc\Delta T$ With no phase change: $q_{system} + q_{surroundings} = 0$



### Pressure-Volume Work Example: Gas Compression

• Piston is compressing a given amount of gas. It exerts a constant force, such that the pressure is 1.1 atm. If the initial volume of the gas in the cylinder was 1.0 L and is compressed it to 0.5 L, how much work was done to compress the gas?

$$W = -P\Delta V$$
  

$$W = -P(V_f - V_i)$$
  

$$W = -1.1 \text{ atm } (0.5 \text{ L} - 1.0 \text{ L})$$
  

$$W = -1.1 \text{ atm } (-0.5 \text{ L})$$
  

$$W = +0.55 \text{ L}\text{-atm}$$

Work was done on the system

# Pressure-Volume Work Example 2: Gas expansion through production • Excess hydrochloric acid is added to an open beaker containing 1 mole of zinc, which produces H<sub>2</sub>. (P = 1 atm, T = 300 K)

A) Provide a balanced chemical reaction.

$$2\text{HCl} + \text{Zn}_{(s)} \rightarrow \text{ZnCl}_2 + \text{H}_2$$

B) How much work is done from this process?

$$\begin{split} \mathbf{W} &= -\mathbf{P}\Delta \mathbf{V} \\ \mathbf{W} &= -\mathbf{P}(\mathbf{V}_{\mathrm{f}} - \mathbf{V}_{\mathrm{i}}) & \underset{\mathbf{P}\mathbf{V} = \,\mathbf{n}\mathbf{R}\mathbf{T}, \, \mathrm{or...} \, \mathbf{V} = \,\mathbf{n}\mathbf{R}\mathbf{T}/\mathbf{P} \\ \mathbf{W} &= -\mathbf{P}(\mathbf{n}_{\mathrm{f}}\mathbf{R}\mathbf{T}_{\mathrm{f}}'\mathbf{P} - \mathbf{n}_{\mathrm{i}}\mathbf{R}\mathbf{T}_{\mathrm{i}}'\mathbf{P}) \\ \mathbf{W} &= -\mathbf{R}\mathbf{T}(\mathbf{n}_{\mathrm{f}} - \mathbf{n}_{\mathrm{i}}) & \underset{\mathbf{V} = -\mathbf{R}\mathbf{T}\Delta\mathbf{n} \\ \mathbf{W} &= -\mathbf{R}\mathbf{T}(1.0 \, \operatorname{mole} - 0 \, \operatorname{mole}) \\ \mathbf{W} &= -2.48 \, \mathrm{kJ} \end{split}$$

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### Pressure-Volume Work Example 3: Reversible Isothermal Expansion

- Imagine that the pressure in a cylinder is the same as the external pressure. If the external pressure increases just a bit, the piston will move to compress the gas. The opposite is also true. When this happens without a temperature change, it is an example of a reversible isothermal process.
- Remember that  $\overline{W} = \int \vec{F} \cdot d\vec{r}$ , where F = PA
- This can be re-written as  $W = \int -P dV$ , where P = nRT/V

$$W = \int -\frac{nRT}{V} dV$$

$$W = -nR$$
  $\frac{1}{V}dV$ 

 $W = -nRT \ln \frac{V_f}{V_i}$ 

This represents the MOST work that can be achieved from a process.

# The First Law of Thermodynamics The total energy of an isolated system is constant. Energy can be transformed from one form to another, but cannot be created or destroyed. The is described by the following equation: $\Delta U = Q + W$ AU - internal energy of the closed system Q - the heat supplied to the system W - the work done on the system







<b>FIU</b> Enthal	ру	
	H = U + PV	
•This is true for any system (not just a perfect gas).		
•Like U, P, and V, enthalpy	(H) is a state function.	
-This means that we don't destination.	care about the path taken, only the origin and	
• Changes in enthalpy therefore can be expressed as: $\Delta H = \Delta U + \Delta (PV)$		
•If constant Pressure:	$\Delta H = \Delta U + P \Delta V$	
• Remember though that:	$\Delta U = q - P \Delta V$	
•Therefore:	$\Delta H = q$	
•This is not unexpected, but means that we can express enthalpy as a transfer of heat between the system and surroundings 15		





### Temperature Dependence of the Enthalpy

	$C_P = \frac{\Delta H}{\Delta T}$ , or $C_P = \left(\frac{\partial H}{\partial T}\right)_P$	
Es	stimation: $C_P = a + bT + \frac{1}{T}$	<u>c</u> 2
Remember:	$\Delta H = \Delta U + \Delta (PV)$	
This means that enthalpy	will always be greater than	the internal energy.
Recall also that for a perfe	ect gas PV=nRT	
Therefore, for one mole:	$\Delta H = \Delta U + \Delta (RT)$	
	$\frac{\Delta H}{\Delta T} = \frac{\Delta U}{\Delta T} + R$	

Rearranged, this becomes:  $C_P - C_V = R$ 

**Physical Change** 

- Phase: A state of Matter (Solid, Liquid, Gas)
- •The standard state of a substance is the pure substance at 1 bar (100 kPa)
- •We use a superscript ' ' to denote standard state

•A phase transition is when the state of matter of a substance changes

 $H_2O(s) \rightarrow H_2O(l) \Delta H^{\Theta} = 6.01 \text{ kJ/mol}$ 

•The reverse reaction will therefore have the opposite enthalpy change  $H_2O(l) \rightarrow H_2O(s) \Delta H^{\Theta} = -6.01 \text{ kJ/mol}$ 





## **Combining Enthalpy Changes**

- •Remember, enthalpy is a state function. The path is irrelevant!
- •The path may be helpful though as we may not be able to directly measure the enthalpy as a single step.

$$Mg_{(s)} \rightarrow Mg^{2+}_{(g)}$$





## The Enthalpy of Chemical Changes

Some definitions:

Bond dissociation - The process of breaking a chemical bond

 $HCl \rightarrow H + Cl \quad \Delta H^{\bullet} = 431 \text{ kJ/mol}$ 

This is known as the bond enthalpy

• Breaking chemical bonds requires energy

• Making chemical bonds releases energy Na + Cl  $\rightarrow$  NaCl  $\Delta H^{\bullet} = -411 \text{ kJ/mol}$ 

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# Not all bonds are created equal, and, every O-H bond for example is different, depending upon the rest of the molecule. H<sub>2</sub>O → H + OH, ΔH\* = 499 kJ/mol, this involves breaking one O-H bond OH→ H + O, ΔH\* = 428 kJ/mol, this involves breaking one O-H bond We often average the bond enthalpies from a variety of molecules to determine the mean bond enthalpy. In this case, we would conclude that the O-H mean bond enthalpy is: (499+428)/2 kJ/mol, or 463 kJ/mol This is useful when examining a new reaction where data may not be available.

# First transforms A $\Rightarrow$ B (for example). Hess stated: The standard enthalpy of a reaction is the sum of the standard enthalpies of the reactions into which the overall reaction may be divided. $\Delta H_{rxn} = \Sigma H_{rxns}$ For A $\Rightarrow$ B $\Rightarrow$ C $\Rightarrow$ D $\Delta H_{A,>D} = \Delta H_{A,>B} + \Delta H_{B,>C} + \Delta H_{C,>D}$ This is not new to us, though this is a new way of thinking about it.







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### First Law – Worked Example

Determine the Enthalpy of the following reaction:  $CH_{4(g)} + 2 O_{2(g)} \rightarrow CO_{2(g)} + 2 H_2O_{(l)}$ 

Approach 1: Mean bond enthalpies

Bonds Broken: $2O_2 \rightarrow 4 \text{ O}$  $\Delta H = 994 \text{ kJ} (2 \text{ mol} \times 497 \text{ kJ/mol})$  $CH_4 \rightarrow C + 4 \text{ H}$  $\Delta H = 1740 \text{ kJ} (4 \times 435 \text{ kJ/mol})$ Bonds Formed: $C + 2O \rightarrow CO_2$  $AH = -1486 \text{ kJ} (2 \times -743 \text{ kJ/mol})$  $4H + 2O \rightarrow 2H_2O$  $\Delta H = -1968 \text{ kJ} (4 \times -492 \text{ kJ/mol})$ 

 $\label{eq:2.1} \begin{array}{l} \Delta H_{\rm r} = 994 +\! 1740 \! \cdot \! 1486 \! \cdot \! 1968 \; kJ/mol \\ \Delta H_{\rm r} = -720 \; kJ/mol \end{array}$ 



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### Variation of Reaction Enthalpy with Temperature



### Worked Example of The Variation of Reaction Enthalpy with Temperature

What is the enthalpy of the following gas-phase reaction at 80 °C:  $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ Solution:  $\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_P dT$   $\Delta H_{80C} = \Delta H_{25C} + \Delta C_P \Delta T$   $\Delta H_{80C} = -241.82 \text{ kJ mol}^{-1} + (-9.945 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})(80 \text{ C} - 25 \text{ C})$   $\Delta H_{80C} = -241.82 \text{ kJ mol}^{-1} - 0.547 \text{ kJ mol}^{-1}$  $\Delta H_{80C} = -242.37 \text{ kJ mol}^{-1}$