

## Chemistry 120

### Thermodynamics

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## Physical Chemistry

- Seeks to frame the Natural World in Terms of Mathematics
- Seeks to write "Equations of State" that describe all Matter and its Interactions
- These Equations of State involve
  - Volume ( $V$ )
  - Pressure ( $p$ )
  - Temperature ( $T$ )
  - Amount of material ( $n$ )

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## Thermodynamics

- Study of Interaction of Matter and Energy
- Questions whether a Chemical Reaction can occur, not if It does
- Need to define a System and the Surroundings
  - *System* part of the universe of interest
  - *Surroundings* rest of the universe

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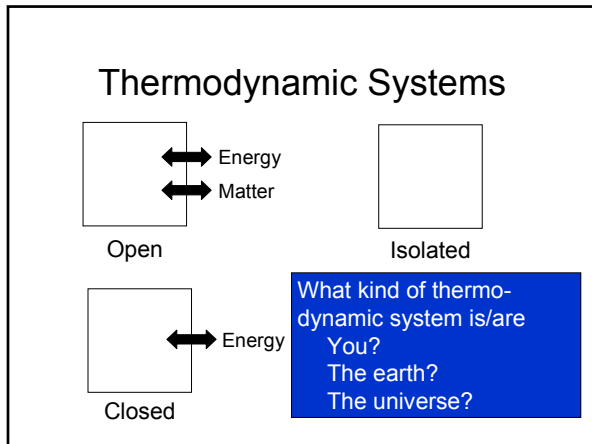
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- ### Energy
- The Mover of Matter
  - Ability to do Work,  $w$ 
    - Apply a force,  $F$ , through a distance,  $d$ , or  
 $w = F \cdot d$
  - Units of Energy
    - Calorie (cal) energy needed to raise 1.00 g  $H_2O$  from 14.5 °C to 15.5 °C.
    - 1 Joule (J) = 1 kg·m<sup>2</sup>·s<sup>-2</sup>
    - 1 cal = 4.184 J
    - 1000 J = 1 kJ

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- ### Types of Energy
- *Kinetic Energy* ( $E_{kin} = 1/2 \cdot m \cdot v^2$ )  
associated with Movement
    - Mechanical energy (sound)
    - Thermal energy (chaotic particle motion)
  - *Potential Energy* associated with  
Object's Position
    - Gravitational energy
    - Electrostatic energy
    - Chemical bonds

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## Transferring Energy

- *Work* is Transfer of Energy using Organized Motion of Particles
  - Application of a force must be concerted
- *Heat* is Transfer of Energy by chaotic Motion of Particles or Radiation
  - *Conduction*
  - *Convection*
  - *Radiation*

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## Work

- Types of Work
  - Expansion work ( $w = -p \cdot \Delta V$ )
  - Non-expansion work (electrical current)
- Sign Convention on Work
  - $w < 0$  system does work (energy leaves system and goes to surroundings)
  - $w > 0$  work is done on the system (energy enters system from surroundings)

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## Heat

- *Temperature* is System's Average *Thermal Energy*
  - Total and average thermal energy not same
- Define a Sign Convention for Heat ( $q$ )
  - $q > 0$  heat enters system (*endothermic*)
  - $q < 0$  heat exits system (*exothermic*)
- Heat Flow
  - Direction of *spontaneous change*
  - *Thermal equilibrium*

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## State Functions

- Thermodynamic Properties that depend on only starting and ending States and not on how States were reached
- Properties
  - Change in state function,  $\Delta = \text{final} - \text{initial}$
  - Changing direction of process, changes sign of  $\Delta$
  - Any change can be broken down into steps, which can be summed to give overall change (*Hess's Law*)

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## State Functions

- Internal Energy ( $U$ )
  - Sum of system's potential and kinetic energy
- Enthalpy ( $H = U + p \cdot V$ )
  - Related to potential energy of system
- Entropy ( $S = k \cdot \ln \Omega$  or  $dS = dq_{rev}/T$ )
  - Describes energy distribution within system
- Gibbs Energy ( $G = H - T \cdot S$ )
  - Related to non-expansion work
  - And spontaneous change at constant  $p$

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## First Law of Thermodynamics

$$\Delta U = q + w$$

- Change in System's Internal Energy must be matched by Heat and Work exchanged with Surroundings
- Only permissible Changes are those that satisfy this Equation
  - Permissible:  $\Delta U = +15 \text{ J}$ ,  $q = +8 \text{ J}$ ,  $w = +7 \text{ J}$
  - Not permissible:  $\Delta U = +15 \text{ J}$ ,  $q = w = +7 \text{ J}$
  - Zero is a valid value for  $\Delta U$ ,  $q$  or  $w$ !

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## Enthalpy

- At constant  $p$ ,  $q_p = \Delta H$ 
  - $q > 0$ ,  $\Delta H > 0$  endothermic
  - $q < 0$ ,  $\Delta H < 0$  exothermic
- Importance of  $\Delta H$ 
  - When  $w = 0$  at constant  $p$  then  $\Delta U = \Delta H$ , so it tells us whether products or reactants are lower in energy
  - With Gibbs energy ( $\Delta G$ ) and entropy ( $\Delta S$ ) is a fundamental chemical thermodynamic property  $\Rightarrow$  bonding

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## Heat Capacity

- Defined as First Derivative of  $q$  with respect to  $T$  at either
  - Constant volume,  $C_v$  ( $q_v = \Delta U$ )
  - Constant pressure,  $C_p$  ( $q_p = \Delta H$ )
- Specific Heat Capacity,  $C$ 
  - Heat required to raise 1 g of substance 1 K
  - For chemists usually at constant pressure
  - Determined from  $C_p$  and molar mass
- Watch Units!

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## Calorimetry

- How  $\Delta H$  and  $\Delta U$  are measured
  - For chemistry  $\Delta H$  is more important
- Constant Pressure Calorimeter
  - Open to air so expansion work possible
  - $q_p = \Delta H$
- Constant Volume (Bomb) Calorimeter
  - Closed system so  $\Delta V = 0$ , so  $w = 0$
  - $q_v = \Delta U$
  - Can convert  $\Delta U$  to  $\Delta H$ ,  $\Delta H = \Delta U + \Delta n \cdot R \cdot T$

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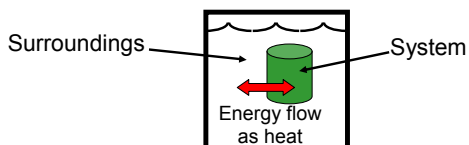
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## Ideal Calorimeter

- Assume that System is Closed and no Work done
  - Energy enters/leaves, matter stays put
- Assume System and its Surroundings do not interact with rest of Universe



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## Calorimetry

- *Calorimeter Constant, C*
  - Specific heat capacity of “real calorimeter” and everything in it
  - Accounts for imperfect nature of real system
- Central Equation for Calorimetry

$$q_{\text{system}} = -q_{\text{surroundings}}$$

- Determining  $q$  at constant  $p$ 
  - From  $\Delta H$  ( $q = n \cdot \Delta H$ )
  - Or from  $C_p$  or specific heat ( $q = m \cdot C \cdot \Delta T$ )

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## Calorimetry Problem Solving

- Start with Equation:  $q_{\text{system}} = -q_{\text{surroundings}}$ 
  - Be careful defining system and surroundings
  - In solution the system is virtual!
- Find equations for  $q_{\text{system}}$  and  $q_{\text{surroundings}}$ 
  - Either  $q = n \cdot \Delta H$ , or  $q = m \cdot C \cdot \Delta T$
  - Only four possible combinations!
- Solve for unknown Quantity
  - Watch signs (include ‘+’ when needed) and units!

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### Calorimetry Problem

- If a 50.0 g piece of Fe at 100.0 °C is placed into 200.0 g H<sub>2</sub>O at 20.0 °C, and allowed to come to thermal equilibrium. What is the final temperature?

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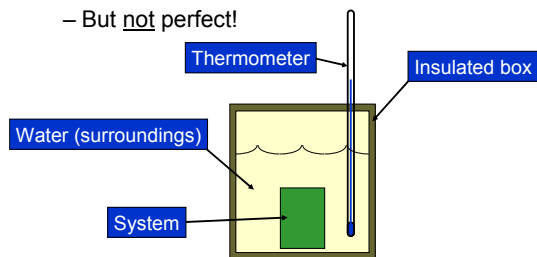
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### Real-World Calorimetry

- Real Calorimeters are designed to minimize Heat Loss
  - But not perfect!



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### Solution Calorimetry

- Performed at *Constant Pressure*
  - Measure  $\Delta H_{rxn}$  directly since  $q_p = \Delta H_{rxn}$
- In an Ideal Calorimeter Reaction
  - Heats/cool only solution and solutes
- In a Real Calorimeter Reaction
  - Heats/cool only solution and solutes
  - Also heats/cool calorimeter itself
- Real Calorimeters are leaky
  - Energy passes into/out of calorimeter
  - Matter also can pass (albeit negligible)

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## Solution Calorimetry

- Start with  $q_{rxn} = -q_{calorimeter}$ 
  - Remember  $q_{calorimeter}$  includes the solution, the products, any excess reactants (and the calorimeter if not ideal)
- Equation for  $q_{rxn}$  is  $q_{rxn} = n \cdot \Delta H_{rxn}$ 
  - Where  $n$  is moles of limiting reagent
- And for Calorimeter,  $q_{calorimeter} = C_{cal} \cdot m \cdot \Delta T$ 
  - Where  $C_{cal}$  is calorimeter constant
  - $m$  is mass of calorimeter and everything in it

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## Solution Calorimetry

- Procedure for a Real Calorimeter
  - Measure  $\Delta T$  for a reaction with a known  $\Delta H$  (must know limiting reagent)
  - Determine  $C_{cal}$
  - Then measure  $\Delta T$  for a reaction with an unknown  $\Delta H$  (limiting reagent)
  - Calculate  $\Delta H$  for the reaction
- Procedure is similar for Bomb Calorimetry
  - Added twist is conversion  $\Delta U$  to  $\Delta H$

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## Solution Calorimetry Problem

- Find the final temperature of the solution formed when 11.02 g of NaCl is dissolved in 125.0 g of water initially at 23.1 °C. The formula weight of NaCl is 58.443 g/mole. Assume that the calorimeter is perfect and that the solution's specific heat is 4.184 J·g<sup>-1</sup>·K<sup>-1</sup>.

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## Enthalpy and Physical Change

- Energy is required for or released during a Physical Change
  - Boiling/condensing (gas/liquid)  $\Delta H_{vap}$
  - Melting/freezing (solid/liquid)  $\Delta H_{fus}$
  - Sublimation (solid/gas)  $\Delta H_{sub}$
  - Dissolution  $\Delta H_{diss}$
- Forces that hold Atoms/Molecules in a Particular State must be overcome
- Conditions Matter!

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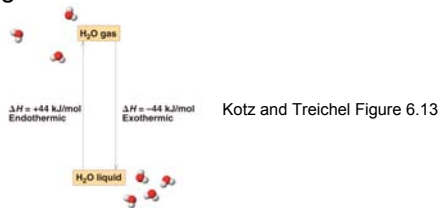
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## $\Delta H$ for State Change

- Defined as being Positive
  - Remember to switch sign for reverse process
- Example:  $\Delta H_{vap}$ : positive for vaporization, negative for condensation




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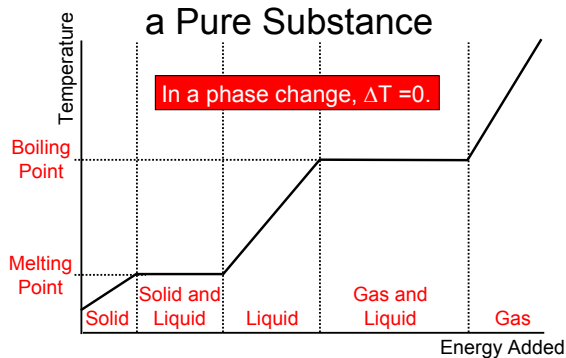
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## Heating Curve for a Pure Substance




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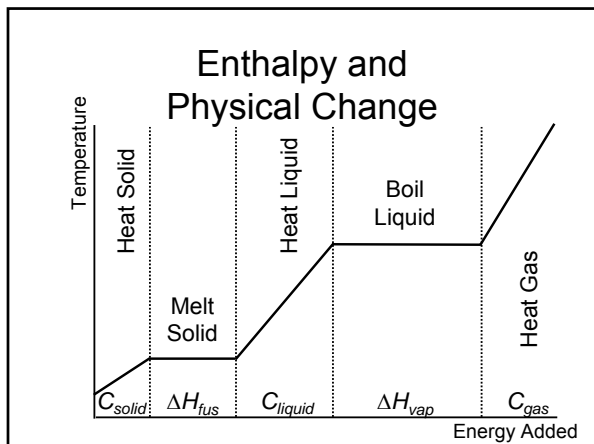
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### Enthalpy and Physical Change

- How much heat is required when 100.0 g of water is heated from its melting point and converted completely to steam at 100.0 °C? The molar mass of water is 18.015 g/mol,  $C_{\text{water}} = 4.184 \text{ J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$ , and  $\Delta H_{\text{vap}} = +40.7 \text{ kJ/mole}$ .

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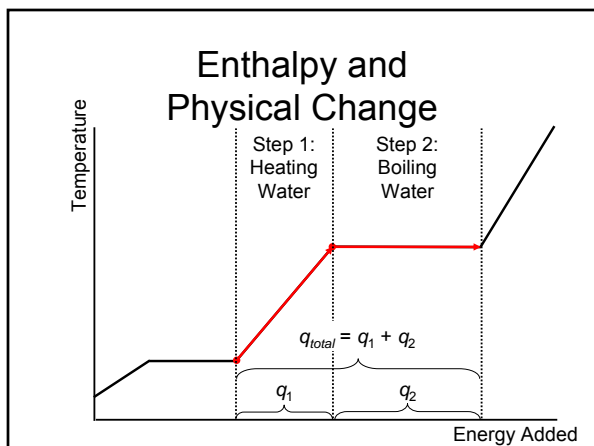
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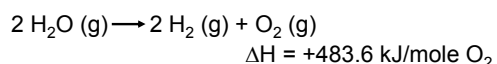
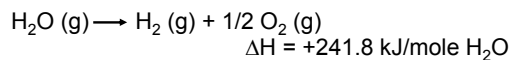
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## Enthalpy and Chemical Change

- All Chemical Changes have a  $\Delta H$ , where  $\Delta H = H_{\text{products}} - H_{\text{reactants}}$  as written
  - Reversing reaction changes sign of  $\Delta H$
- For a Reaction  $\Delta H$  always associated with macroscopic Quantity of Moles



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## Enthalpy and Chemical Change

- The enthalpy of combustion ( $\Delta H_{\text{comb}}$ ) for  $\text{C}_3\text{H}_8$  is -2220. kJ/mole. If 200.0 g  $\text{C}_3\text{H}_8$  is burned, how much heat is released?  
Molar mass of  $\text{C}_3\text{H}_8 = 44.096 \text{ g/mole}$ .

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## Enthalpy as a State Function

- Hess's Law
- *Standard Reaction Enthalpies*,  $\Delta H_{\text{rxn}}^0$ 
  - Measured at 1 bar pressure
  - Commonly tabulated values at 25 °C
- *Standard Molar Enthalpies of Formation*,  $\Delta H_f^0$ 
  - At 1 bar pressure (and usually 25 °C)
  - Forming one mole of compound from its elements in their reference states

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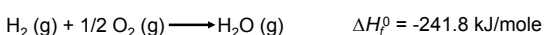
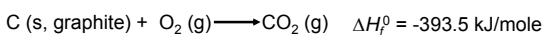
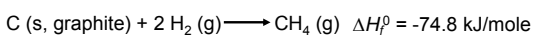
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### Hess's Law

- If a Reaction can be written as the Sum of other Reactions,  $\Delta H$  for the Reaction is the Sum of  $\Delta H$  for these other Reactions
  - Example: determine  $\Delta H^\circ$  for the combustion of methane from the reactions



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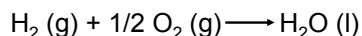
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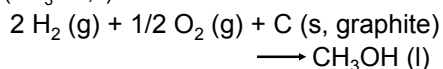
### Using $\Delta H_f^\circ$

- Examples of Reactions that define  $\Delta H_f^\circ$ 
  - May not be able to do the reaction!
  - Note: can also define  $\Delta H_f$  at non-standard conditions

$\Delta H_f^\circ(\text{H}_2\text{O, l}) = -285.8 \text{ kJ/mole}$  is  $\Delta H^\circ$  for the reaction



$\Delta H_f^\circ(\text{CH}_3\text{OH, l}) = -238.66 \text{ kJ/mole}$  is for the reaction



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### Standard Molar Enthalpies of Formation

- For elements  $\Delta H_f^\circ = 0$ 
  - Element is in its reference state (*allotrope*)
  - Example: most stable allotrope of C is graphite so  $\Delta H_f^\circ(\text{C, s, graphite}) = 0$
  - Exceptions
- Values of  $\Delta H_f^\circ$  depend on Substance's State
  - Example:  $\Delta H_f^\circ(\text{H}_2\text{O, l}) \neq \Delta H_f^\circ(\text{H}_2\text{O, g})$  at some  $T$

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### Using $\Delta H_f^0$ to Predict $\Delta H$ for a Reaction

- Tabulated  $\Delta H_f^0$  can be used to predict  $\Delta H_{rxn}^0$  for any Reaction
  - Can also predict  $\Delta H_{rxn}$  at non-standard conditions
- Sum  $\Delta H_f^0$  for Products, subtract sum of  $\Delta H_f^0$  for Reactants
  - Multiply by stoichiometric coefficients

$$\Delta H_{rxn}^0 = \sum[\Delta H_f^0(\text{products})] - \sum[\Delta H_f^0(\text{reactants})]$$

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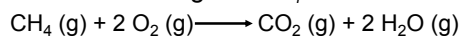
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### Using $\Delta H_f^0$ to predict $\Delta H_{rxn}^0$

- Determine  $\Delta H_{rxn}^0$  for the reaction shown below from the given  $\Delta H_f^0$ .



$$\Delta H_f^0(\text{CH}_4, \text{g}) = -74.8 \text{ kJ/mole}$$

$$\Delta H_f^0(\text{CO}_2, \text{g}) = -393.5 \text{ kJ/mole}$$

$$\Delta H_f^0(\text{H}_2\text{O}, \text{g}) = -241.8 \text{ kJ/mole}$$

$$\Delta H_f^0(\text{O}_2, \text{g}) = 0 \text{ kJ/mole}$$

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### Summary to this Point

- Can measure Energy changes associated with Chemical Reactions and Physical Change
- Can predict Heat absorbed/given off by Chemical and Physical Changes
- Cannot predict whether a Process is Spontaneous
  - There are spontaneous endothermic reactions!

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## Spontaneity and Thermodynamics

- First Law
  - Shows *permissible* changes
  - But not which permissible changes are spontaneous
- Other Considerations
  - What is distribution of energy within system?
  - What is the probability that some particular arrangement is accessible?

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## Entropy

- Entropy ( $S = k \cdot \ln \Omega$ , units  $\text{J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$ )
  - Where  $\Omega$  = number of different ways particles in system can be arranged (*microstates*)
  - Describes energy distribution
  - Also degree of order/disorder within system
- Define  $\Delta S = S_{\text{final}} - S_{\text{initial}}$ 
  - Just like  $\Delta H$  and  $\Delta U$  for switching direction
- *Nernst Heat Theorem*
  - For any change  $\Delta S \rightarrow 0$  as  $T \rightarrow 0 \text{ K}$

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## Second Law of Thermodynamics

- In an *isolated* System any spontaneous Change must have  $\Delta S > 0$ 
  - For universe  $\Delta S > 0$  always
- For *non-isolated* Systems
  - $\Delta S_{\text{system}} = -\Delta S_{\text{surroundings}}$
  - So  $\Delta S_{\text{system}} < 0$  possible since  $\Delta S_{\text{surroundings}} > 0$
  - $S_{\text{universe}}$  increases, as required by Second Law
  - Order increases in system at the expense of disordering the universe

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### Third Law of Thermodynamics

- If  $S$  of every Element in its most stable State at  $T = 0$  K is defined as 0, which it is for all perfect crystalline Substances, then  $S$  for every Substance is positive.
  - At 0 K, a perfect crystalline solid has only one state accessible ( $\Omega = 1$ ), so  $S = 0$
  - Follows from Nernst Heat Theorem
- Can define  $S$  for all Substances
  - Note difference with  $H$  and  $U$ !

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### Third-Law Entropies

- By choosing  $S$  at 0 K to be 0, can define a set of *Third-Law Entropies*
  - Often referred to as *standard entropies*,  $S^\circ$
  - Tabulated values usually at 25 °C
  - Temperature specified, because  $S(T)$
- Because  $S$  is a State Function, can calculate  $\Delta S$  for a Reaction by
$$\Delta S_{rxn}^\circ = \sum[S^\circ(\text{products})] - \sum[S^\circ(\text{reactants})]$$

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### More on Entropy

- $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$  for the same, or similar, Substances
- $S$  is greater for more Complex Molecules
  - $S$  increases as number of atoms increases
  - $S$  larger for more complex structures with the same number of atoms
- $\Delta S$  is positive when
  - Homogeneous mixture formed
  - Gas is generated

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## Relationship between $S$ and $U$

- $U$  is the total Energy,  $S$  tells how that Energy is distributed, but how does this relate to  $H$  and Spontaneity?
  - Start with another expression of the Second Law at constant temperature called the *Clausius inequality*.

$$\Delta S \geq \frac{q_{rev}}{T}$$

- At constant  $p$  and  $T$  with  $w = 0$ , this becomes  $0 \geq \Delta H - T\Delta S$

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## Gibbs Energy

- Define the Gibbs Energy:  $G = H - T \cdot S$ 
  - State function
  - Total non-expansion work system can do
  - Very useful for chemists, as signpost for spontaneity of a chemical reaction
- At constant Temperature and Pressure Expression for  $\Delta G$  is  $\Delta G = \Delta H - T\Delta S$ 
  - Process is spontaneous if  $\Delta G < 0$

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## Gibbs Energy

- For  $\Delta G$  to be negative, either
  - Large and negative  $\Delta H$ , or
  - Large and positive  $\Delta S$ , or
  - With positive  $\Delta H$ , but smaller than  $T\Delta S$
- No Reaction can be Spontaneous if  $\Delta H$  is positive and  $\Delta S$  is negative
  - But can be driven by input of work or coupling to another reaction with  $\Delta G < 0$

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## Gibbs Energy

- Like all State Functions, reversing a Process flips Sign of  $\Delta G$ 
  - A non-spontaneous reaction is spontaneous if run the other way!
- Spontaneity of Reaction may depend on  $T$ 
  - If there exists a  $T$  where  $\Delta H = T\Delta S$  ( $\Delta G = 0$ ), reaction flips its direction
  - Ignores temperature dependence of  $H$  and  $S$
- When  $\Delta G = 0$ , System is at *Equilibrium*

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## Gibbs Energy

- Determined
    - Experimentally from  $\Delta H$  and  $\Delta S$
    - Using  $\Delta H_f^\circ$  and  $\Delta S^\circ$
  - Define a Standard Molar Gibbs Energies of Formation,  $\Delta G_f^\circ$ ,
    - As  $\Delta G$  for reaction that forms one mole of substance from its elements in their reference states
    - For elements in reference state  $\Delta G_f^\circ = 0$
- $$\Delta G_{rxn}^\circ = \sum[\Delta G_f^\circ(\text{products})] - \sum[\Delta G_f^\circ(\text{reactants})]$$

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## Sample Calculations

- What is  $\Delta H$  for this Reaction at 300.0 K and 1 bar of Pressure?

	$\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6 \text{O}_2(\text{g}) \longrightarrow 6 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{l})$			
$\Delta G_f^\circ$ (kJ/mole)	-910.	0	-394.36	-237.13
$S^\circ$ (J/K·mole)	212	205.138	213.74	69.91

Is there any  $T$  at which this reaction is not spontaneous? Ignore the temperature dependence of  $H$  and  $S$ .

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