

Wednesday May 21, 2014

Objective: The student will be able to (1) analyze the Laws of Thermodynamics both qualitatively and quantitatively, and (2) explain sign conventions of state functions.

Homework: Complete Thermodynamics Problem Set #1

Warm - Up: (5 mins)

How much heat (in kJ) energy is required to bring 23.5 grams of ice at -5.00°C to 25.0°C .

ANS: $q_{\text{tot}} = 10.5 \text{ kJ}$

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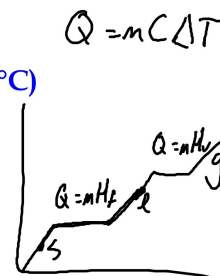
How much heat (in kJ) energy is required to bring 23.5 grams of ice at -5.00°C to 25.0°C .

$$q_1 = mC_p\Delta T \\ = (23.5 \text{ g})(2.05 \text{ J/g}^{\circ}\text{C})(0^{\circ}\text{C} - (-5^{\circ}\text{C})) \\ = 240.875 \text{ J}$$

$$q_2 = mH_f \\ = (23.5 \text{ g})(334 \text{ J/g}) \\ = 7849 \text{ J}$$

$$q_3 = mC_p\Delta T \\ = (23.5 \text{ g})(4.18 \text{ J/g}^{\circ}\text{C})(25.0^{\circ}\text{C} - 0^{\circ}\text{C}) = 10545.625 \text{ J} \\ = 2455.75 \text{ J}$$

$$q_{\text{tot}} = q_1 + q_2 + q_3 \\ = 10.5 \text{ kJ}$$



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Lecture Outline

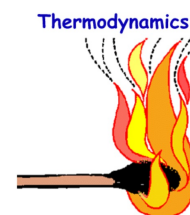
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Thermodynamics and Thermochemistry

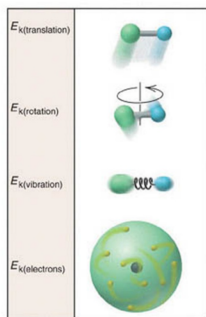
Thermochemistry: the study of the energy and heat associated with chemical reactions and/or physical transformations.

Thermodynamics: branch of natural science concerned with heat and its relation to energy and work.

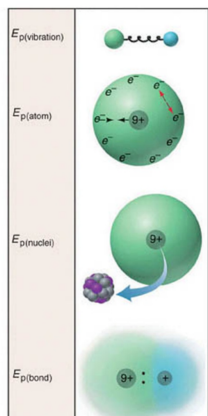


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Types of Energy Contributions

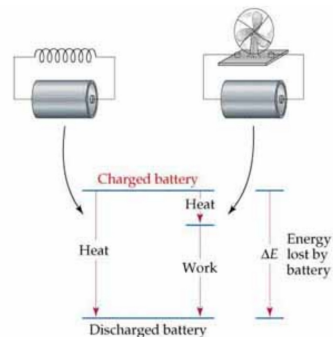


A Contributions to kinetic energy (E_k)



B Contributions to potential energy (E_p)

State Functions

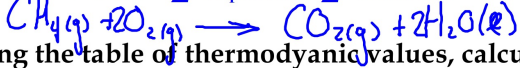


Example: liquid water @ 25°C

Enthalpy (ΔH)

Thermo comes from the greek word for heat.

$$\Delta_{\text{rxn}}H = \sum \Delta H_{\text{products}} - \sum \Delta H_{\text{reactants}}$$

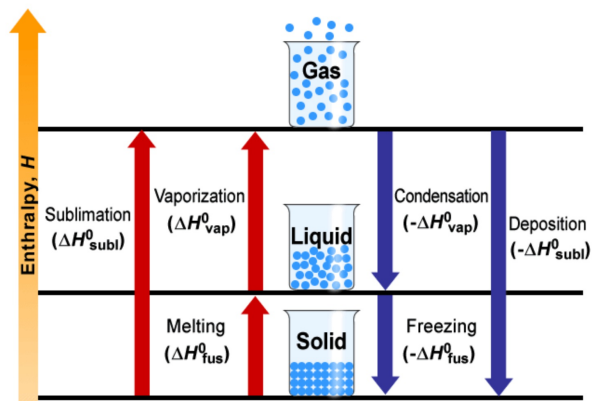


Using the table of thermodynamic values, calculate the heat of reaction for the combustion of methane.

$$\Delta_{\text{rxn}}H = [\Delta_f H_{\text{CO}_2} + 2\Delta_f H_{\text{H}_2\text{O}}] - [\Delta_f H_{\text{CH}_4} + 2\Delta_f H_{\text{O}_2}]$$

$$= [(-393.51 \text{ kJ/mol}) + 2(-285.83)] - [(-74.9) + 2(0)]$$

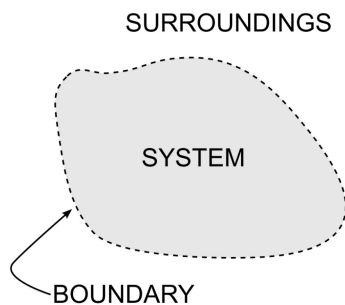
$$\Delta_{\text{rxn}}H = -888 \text{ kJ/mol}$$



Phase Transitions

Systems and Surroundings

A scientific "system" is a defined area based on a study of interest.



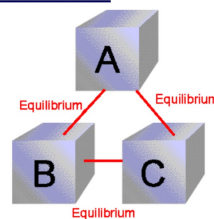
In chemistry, a system is where the reaction takes place.

The Zeroth Law of Thermodynamics

If system A is in thermal equilibrium with system B, and system B is in thermal equilibrium with system C, then system A and system C are also in thermal equilibrium.

The Zeroth Law

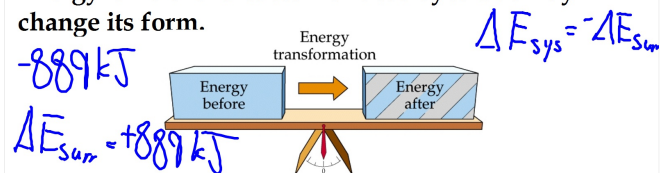
Think of the transitive property in Algebra and mathematics.



The First Law of Thermodynamics

$\Delta E = \Delta H$ (The Law of Conservation of Energy)

Energy is neither created nor destroyed but may change its form.



$$\Delta E_{\text{universe}} = \Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0$$

$$\Delta E_{\text{system}} = q + w$$

The Sign Conventions* for q , w and ΔE

q	+	w	=	ΔE
+		+		+
+		-		depends on sizes of q and w
-		+		depends on sizes of q and w
-		-		-

* For q : + means system gains heat; - means system loses heat.

* For w : + means work done on system; - means work done by system.

Example Problem

A gas in a system absorbs 80 kJ of heat and therefore does 110 kJ of work. What is the energy of the system? The surroundings? The universe?

Handwritten notes:

$$\Delta E = q + w$$

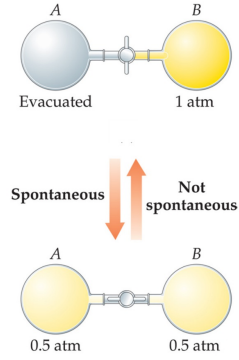
$$= +80 \text{ kJ} + (-110 \text{ kJ})$$

$$\Delta E_{\text{sys}} = -30 \text{ kJ}$$

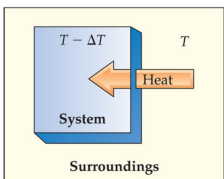
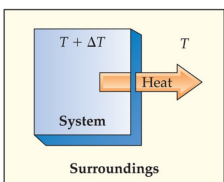
$$\Delta E_{\text{surr}} = +30 \text{ kJ}$$

Additional notes: $\frac{dMg}{dS}$, $\int Ca \frac{dS}{dS}$

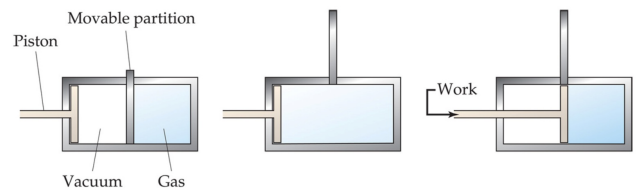
Spontaneous Processes



Reversible Processes

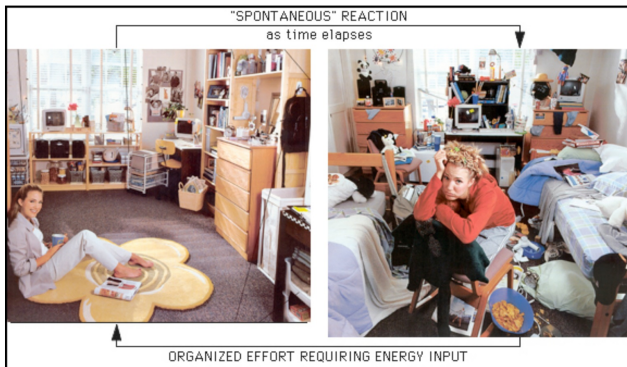


Irreversible Processes

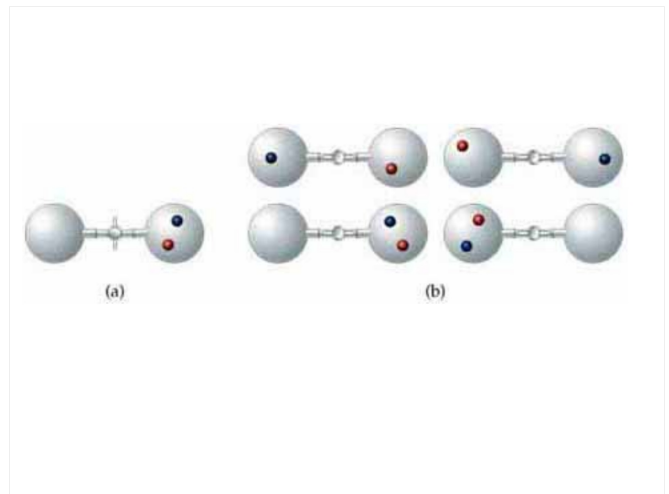


No P-V work, surroundings must do work

Entropy: A concrete example

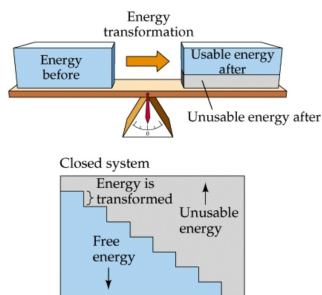


Entropy has to deal with options: the more, the better.



The Second Law of Thermodynamics (The Entropy Law)

All systems tend toward maximum entropy (ΔS).



Entropy is a measurement of disorder in a system.

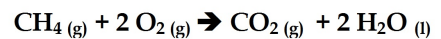
Entropy Calculations

Two methods:

(1) prediction (Δn_{gas})

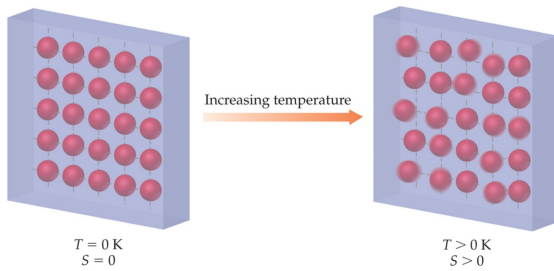
(2) Table of Values: $\Delta_{\text{rxn}}S = \sum \Delta S_{\text{products}} - \sum \Delta S_{\text{reactants}}$

Predict and calculate the value and sign of $\Delta_{\text{rxn}}S$ for the combustion of methane.



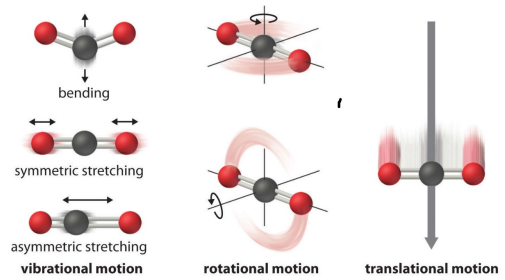
The Third Law of Thermodynamics (The Energy Law)

The entropy (S) of a pure crystalline solid at absolute zero (0 K) is zero (no disorder).



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Summary of the Laws

#	LAW [condensed form]
0 th	The EQUILIBRIUM Principle
1 st	The ENERGY Principle
2 nd	The ENTROPY Principle
3 rd	The TEMPERATURE Principle

Calculate the amount of energy necessary to cool 55.0 grams of liquid water at 100 deg C to -24 deg C.

$$\begin{aligned}
 q_1 &= mC\Delta T \\
 &= 55.0\text{g}(4.18\text{J/g}\cdot\text{oc})(-100\text{oc}) \\
 &= -22990\text{J} \\
 q_2 &= mH_f \\
 &= 55.0\text{g}(-334\text{J/g}) \\
 &= -18370\text{J} \\
 q_3 &= mC\Delta T \\
 &= 55.0\text{g}(2.05\text{J/g}\cdot\text{oc})(-24\text{oc}) \\
 &= -2786\text{J} \\
 q_{\text{tot}} &= -44.1\text{kJ}
 \end{aligned}$$

Sign Conventions for State Functions		
	(+)	(-)
ΔH	unfavorable ENDO (absorbed)	favorable EXO (released)
ΔS	favorable disorder \uparrow	unfavorable disorder \downarrow


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Objective Check

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How are we meeting our objective?



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Thermo Day 2

Objective: The student will be able to (1) justify the spontaneity of reactions with Gibbs Free Energy and (2) apply the Laws of Thermodynamics to direct applications.

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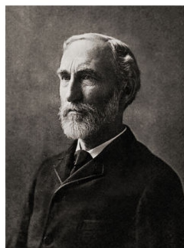
Gibbs Free Energy (ΔG) and Spontaneity

The thermodynamic potential ^{not} that describes the spontaneity of a chemical reaction.

$\Delta G^\circ = \text{naught}$
 ΔG is the ONLY way we can determine the spontaneity of a ~~reaction~~ ^{System}.

Can be calculated multiple ways:

- (1) $\Delta_{\text{rxn}}G = \sum \Delta G_{\text{products}} - \sum \Delta G_{\text{reactants}}$
- (2) $\Delta_{\text{rxn}}G = \Delta_{\text{rxn}}G^\circ + RT \ln Q$
- (3) $\Delta_{\text{rxn}}G^\circ = \Delta_{\text{rxn}}H^\circ - T\Delta_{\text{rxn}}S^\circ$



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Sign conventions of Thermodynamic Potentials

Discuss signs and favorability of ΔH , ΔS , and ΔG .

$$\Delta G = \Delta G^\circ + RT \ln Q$$

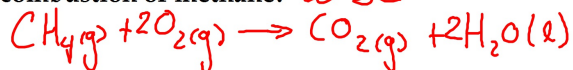
diff. b/w ΔG and ΔG°
↓

Func.	+	-	0
ΔH	ENDO heat abs. unfav.	EXO (fav.) heat released	no heat transferred std. con 1 atm 25°C
ΔS	En. ↑ favorable	En. ↓ unfav.	no change in randomness STP 1 atm 0°C
ΔG	nonspontaneous unfav.	spontaneous fav.	equil.

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-242.79 kJ/mol Gibbs Free Energy Example

What is the free energy associated with the combustion of methane? @ SC



$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

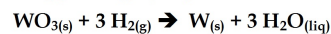
$$= -888 \text{ kJ/mol} - (298 \text{ K} \cdot -0.243 \text{ kJ/mol})$$

$$= -888 \text{ kJ/mol} + 72.414 \text{ kJ/mol}$$

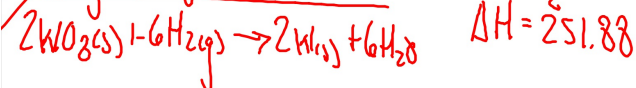
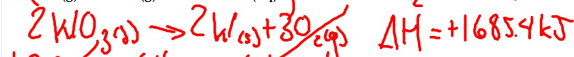
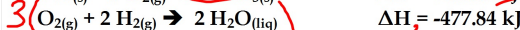
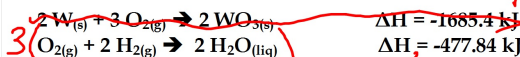
$$= -815.586 \text{ kJ/mol}$$

Applications Hess' Law

Calculate the enthalpy change (ΔH) for the following reaction:



given the following information:



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Applications Calorimetry

mass of metal.....25.0 grams
mass of water in calorimeter.....20.0 grams
temp.of large sample of water.....95.0°C
initial temp. of calorimeter water.....24.5°C
final temp. of calorimeter water.....47.2°C

$$\Delta H_{\text{tot}} = \Delta H_1 + \Delta H_2$$