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Thermochemistry

Chapter 6

Chemistry E1a

Energy: What is it? How is it transformed?

- What is energy? What are the SI units for energy? Give examples of some energy

1.47 J	An apple in a 1 meter tree
230 J	Field Hockey Ball @ 100 mi/hr
3,196 J	1 mole of H ₂ at 298 K
4.32 MJ	Energy in fully charged car battery

- What types of energy are we going to be interested in studying?

Potential Energy: Associated with the position of an object

Kinetic Energy: Associated with the motion of an object

Chemical (Potential) Energy: Associated with the position of electrons and protons in an atom or molecule

Thermal (Kinetic) Energy: Associated with the random motion of a collection of atoms or molecules.

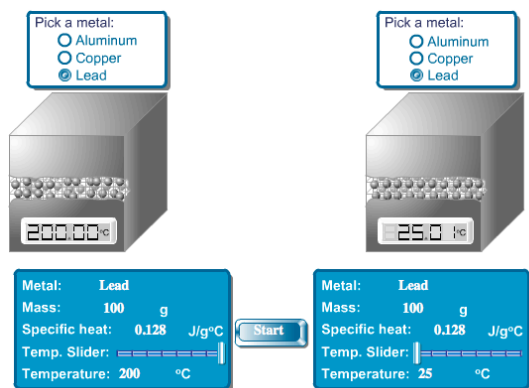
- Are there other forms of energy?
- What about *heat and work*? Are they forms of energy?

Activity 6.01: Thermal Energy and The Flow of Heat

- **Thermal (Kinetic) Energy:** Associated with the random motion of a collection of atoms or molecules.

Below is a picture of two lead blocks each weighing 100g but at different temperatures. The block on the left is at 200°C and the block on the right is at 25°C. Watch the animation and answer the questions. <http://group.chem.iastate.edu/Greenbowe/sections/projectfolder/flashfiles/thermochem/thermoEquiv.html>

- Which object contains more thermal energy? (1) T = 200 °C Block (2) 25 °C Block (3) Both have the same amount of thermal energy
- What do you predict will happen to the atomic motion of the T = 200 °C lead atoms and the T = 25 °C lead atoms when they are brought in contact with each other?



- Will both blocks eventually be at the same final temperature?
- What type of energy is being transferred?
- How is this energy being transferred?

- Heat is a process by which *thermal* energy is transferred from a substance at a high temperature to another substance at a lower temperature. We use the letter q to indicate how much heat was transferred into or out of a substance.

- The amount of heat transferred from the 200 °C lead block to the 25 °C lead block was: $q = -1120 \text{ J}$

- If only the mass of the 200 °C lead block was increased would the amount of heat transferred change: yes or no
- Would this process as described in e cause the lead blocks to have a higher final temperature? yes or no
- If the 200 °C lead block was changed to copper, would the amount of heat transferred change: yes or no

Activity 6.02: Determining the Amount of Heat Gained or Lost

- The equation below used to determine the amount of heat lost or gained by a substance:

$$q = m s \Delta T$$

Heat Lost or gained by a substance → q ← Temperature change of substance $\Delta T = T_{\text{final}} - T_{\text{initial}}$

Mass of substance → m ← specific heat of substance s

- a) Determine how much heat is gained by 100g of lead at 25°C when in contact with 100 g of lead at 200°C after both lead blocks reach a final temperature of $T = 112.50^\circ\text{C}$. Specific heat of lead is $0.128 \text{ J/g } ^\circ\text{C}$

- b) You take an insulated beaker containing 100 g of water at 20°C. You add 50 grams of copper metal that has been heated to 100°C. What will be the final temperature of the system when it reaches thermal equilibrium (everything at the same temperature).

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TABLE 6.2

The Specific Heats of Some Common Substances

Substance	Specific Heat ($\text{J/g} \cdot ^\circ\text{C}$)
Al	0.900
Au	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu	0.385
Fe	0.444
Hg	0.139
H ₂ O	4.184
C ₂ H ₅ OH (ethanol)	2.46

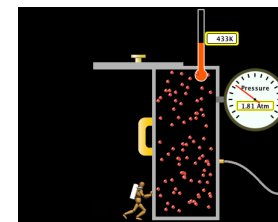
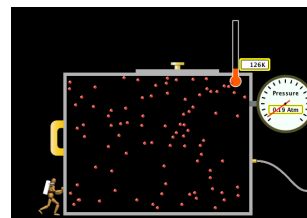
Bonus: Write the first law equation for: 625 g C₂H₅OH at $T = 234^\circ\text{C}$ mixed with 34 g of Al at $T = -23^\circ\text{C}$ mixed with 15 g Au at $T = 50^\circ\text{C}$:

Activity 6.03: Heat and Work are Two Ways of Changing the Temperature of a Gas

a) Lets come back to the animation of our gas. What happens to the average speed of the gas molecules when we increase their temperature?

b) What happens to the average speed of the gas molecules when we decrease the volume of the container?

c) What happens to the average speed of the gas molecules when we increase the volume of the container?



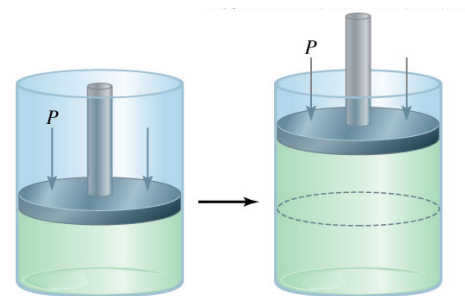
• By increasing or decreasing the volume of a container by moving a wall of the container we are transferring energy into or out of the container. This process of moving a wall and transferring energy is called work. Work (w) is done when a gas expands or contracts against a constant external pressure that causes the wall to move. There is an equation to calculate this transfer of energy:

$$w = - P_{\text{external}} \Delta V$$

Clicker Question:

Determine work (in Joules) for a sample of gas that expands from an initial volume of 1.00 liters to a final volume of 3.50 liters against a constant external pressure of 1.20 atm.

- 1) $w = -3.0 \text{ J}$
- 2) $w = -4.2 \text{ J}$
- 3) $w = -303.9 \text{ J}$
- 4) $w = -425.5 \text{ J}$



Activity 6.05: Internal Energy and Enthalpy

- Lets consider an experiment that takes place in a insulated container. Inside the container is some NH_4Cl and some water. Both the water and the NH_4Cl are at room temperature, 298K, but they are separated by a barrier.

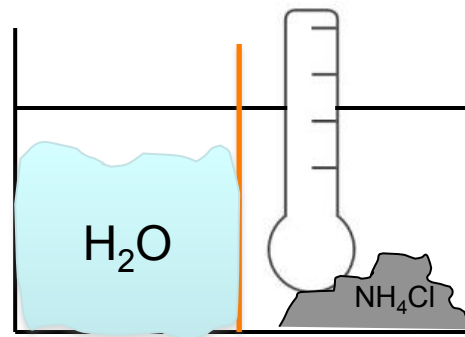
a) When the barrier is removed and the water and the NH_4Cl mix write the first law equation for both substances in contact with each other.

b) Based on the initial temperatures of these two substances what would you expect the value of ΔT for water to be?

1. Negative
2. Zero
3. Positive

- Lets perform the experiment!

Now write the first law equation for when the barrier is removed and the water and the NH_4Cl mixing with water.



Activity 6.04: Work, Heat, and Internal Energy

- We have a way of representing the total energy of a system. The system can be anything you want it to be: a block of lead, a collection of He gas in a balloon, gasoline in the tank of a car. We use the word **internal energy** which is represented by the capital letter **U** to describe the total energy of the system

U = all of the **thermal energy** and **chemical (potential) energy** for a system.

- The U of any system can be changed. The **thermal energy** is changed when you **add remove/heat (q)** or **add/remove work (w)**, the **chemical energy** is changed when the substances in the system undergo a chemical reaction.

So a change in internal energy for any process would be: $\Delta U = q + w$

Sign of ΔU tells us about energy changes: $\Delta U < 0$ Energy is leaving the system. (hot copper in cold water, $\Delta U_{\text{Cu}} < 0$)
 $\Delta U = 0$ No change in energy of the system (copper and water at the same temperature)
 $\Delta U > 0$ Energy is entering the system. (cold copper in hot water, $\Delta U_{\text{Cu}} > 0$)

• Clicker Questions:

An enclosed sample of gas expands against a constant external pressure within a perfectly insulated container so that there is no transfer of heat into or out of the gas.

A. What can you conclude about q for this gas?

- 1) $q < 0$ 2) $q = 0$ 3) $q > 0$

B. What can you conclude about w for this gas?

- 1) $w < 0$ 2) $w = 0$ 3) $w > 0$

C. What can you conclude about ΔU for this gas?

- 1) $\Delta U < 0$ 2) $\Delta U = 0$ 3) $\Delta U > 0$

State Functions: Enthalpy

a) Does the distance you travel to the top of the mountain depend upon your path

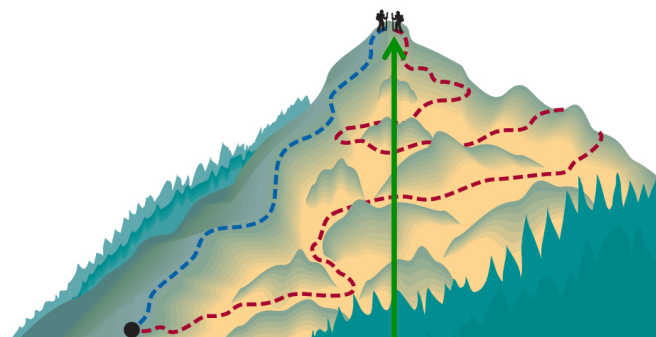
Yes or No

b) If you climbed straight up the mountain following the green path your change in altitude would be 525 feet. If you followed the blue or red path would your change in altitude be the same?

Yes or No

State functions do not depend upon the path taken to reach the value of the function. For example: Altitude is a state function. The difference in altitude that a hiker experiences is not dependent upon the path the hiker took to the top of the mountain. However, distance to the top of the mountain does depend on the path, so distance is not a state function.

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Circle the state functions from this list: T V q P w U R

The equations below are the results of a short derivation starting with the equation $\Delta U = q + w$ and finding an expression under conditions of (1) constant volume and (2) constant pressure.

Under conditions of constant volume:

$$\Delta U = q_v$$

Under conditions of constant pressure:

$$\Delta H = q_p$$

- Where ΔH is a new state function defined in terms of U, P and V. Why would anyone want to create a new state function?

Enthalpies of Reaction (Part 1)

- Consider the following reaction, the combustion of methane:



The “per mole” in the units of ΔH for the reaction above means *per mole of the reaction as it is written with the stoichiometric coefficients above*

$$\text{Number of moles of reaction, } n_{\text{rxn}} = \frac{\text{Number of moles of any reactants that are consumed or any products that are formed}}{\text{Coefficient in the Balanced Chemical Reaction}}$$

- Clicker Question:**

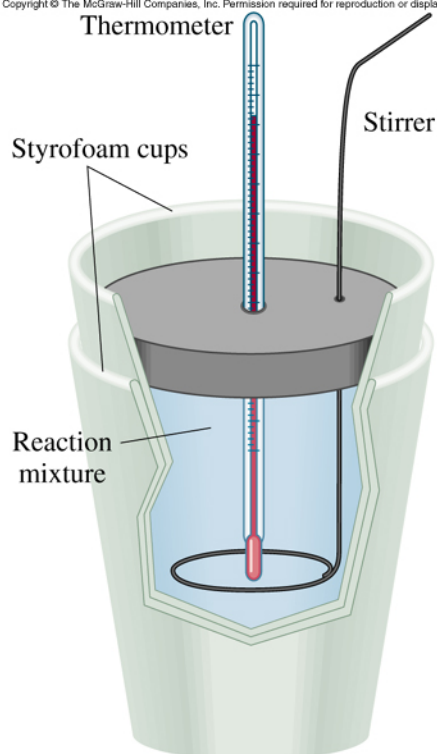
How much heat will be released if 3 moles of $\text{CH}_4(g)$ are mixed with 5 moles of $\text{O}_2(g)$ and this reaction proceeds to completion?

- 1) 1780 kJ of heat released
- 2) 2225 kJ of heat released,
- 3) 2670 kJ of heat released,
- 4) 4450 kJ of heat released,
- 5) 7120 kJ of heat released

Measuring the Enthalpies of Reaction I: Calorimetry Constant Pressure

- We can measure the *enthalpy of reaction* (“heat released per mole of reaction”) by using a technique called calorimetry. This is a closed container specifically designed for this purpose. Here is an example of high tech, expensive version:

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Here is an example of how calorimetry can be used to find ΔH ?

100 ml solutions of 1.00 M NaCl and 1.00 M AgNO₃ are both at a temperature of 22.4°C. These solutions are mixed together in a coffee cup calorimeter and the resulting solution reaches a temperature of 30.2°C. Assume the density of the resulting solution is 1.0 g/ml. The specific heat of the resulting solution is 4.184 J/g°C. Determine the ΔH for this reaction?

Hint: start this problem by writing the first law expression for this process.

Measuring the Enthalpies of Reaction II: Constant Volume Calorimetry

- When measuring the enthalpies of reactions for solids and gasses we use a constant volume calorimeter. This is called a bomb calorimeter. We can determine the q for the calorimeter via below:

$$q_{\text{cal}} = C_{\text{cal}} \Delta T$$

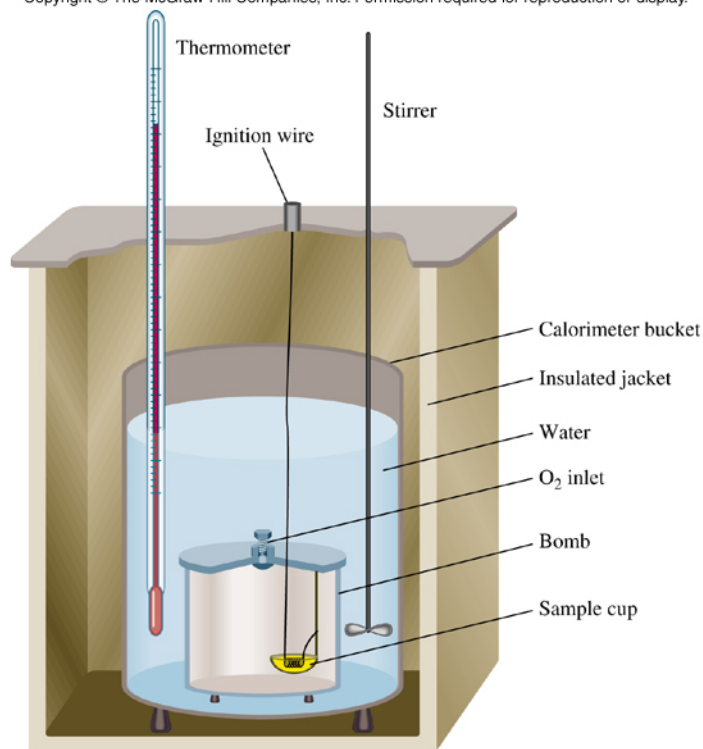
Heat Lost or gained by a calorimeter

Heat capacity of calorimeter

Temperature change of calorimeter
 $\Delta T = T_{\text{final}} - T_{\text{initial}}$

- a) Phosphorus can be burned in oxygen to form P_4O_{10} . When a sample of phosphorus is burned in a bomb calorimeter a 2.187 K rise in temperature is measured. If the heat capacity of the calorimeter is 11.29 kJ/K determine the amount of heat from the reaction that was transferred to the calorimeter.

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Enthalpies of Reaction From Calculation: Hess' s Law


a) Consider hiking up the mountain depicted on this page over three days. (It's the same mountain as before!)

Here is your change in altitude for each day of hiking

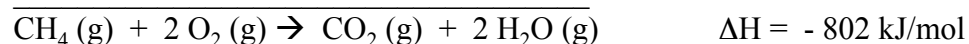
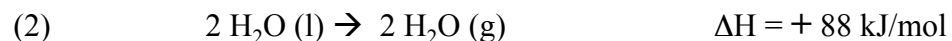
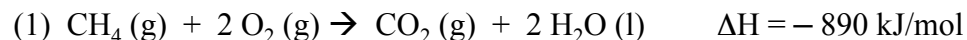
Day 1: Change in altitude is + 220 feet

Day 2: Change in altitude is + 130 feet

Day 3: Change in altitude is + 175 feet

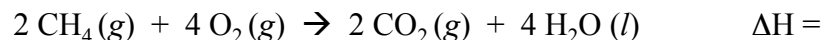
You can find the total change in altitude for the trip by adding the change for each day? 

b) True or False: **Reactions** and **enthalpies** can be added as in the example below where reaction (1) and (2) are added as well as having their enthalpies added.

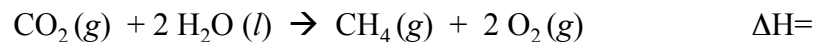


- Here are some properties of changes in enthalpies for chemical reactions

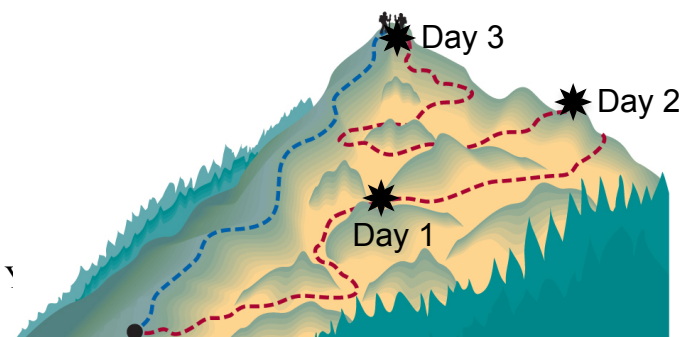
If we multiply a reaction by any number we need to multiply the enthalpy by that same number. If we multiply reaction (1) by 2 we get:



If reverse a reaction we reverse the sign of the enthalpy change



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Enthalpies of Reaction From Calculation: Hess's Law

Hess' s law: "The overall enthalpy of a process is the sum of the enthalpies from **any** series of reactions that, taken together, transform the desired reactants into the desired products" [Munowitz, 2000]

a) Using what you know about reactions and enthalpies from the pervious page solve the following (exam!) problem

Given the following data:



Determine the change in enthalpy (ΔH°) for the following reaction:



Enthalpies of Reaction and Formation Reactions

- Enthalpies of every kind of reaction can be tabulated. For example:
 - Enthalpy of combustion:* $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$ $\Delta H_{\text{comb}} = -890 \text{ kJ/mol}$
 - combustion of 1 mole of a substance
 - Enthalpy of fusion* (melting) $\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{l})$: $\Delta H_{\text{fus}} = 6.01 \text{ kJ/mol}$
 - 1 mole of a substance changing from solid to liquid
 - Occurs at melting point temperature of substance and the temperature remains at the melting point until the substance has completely melted.
 - Enthalpy of vaporization* (boiling): $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$ $\Delta H_{\text{vap}} = 44 \text{ kJ/mol}$
 - 1 mole of a substance changing from liquid to gas
 - Occurs at boiling point temperature of substance and the temperature remains at the boiling point until the substance is completely vaporized.
 - Enthalpy of formation:* $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$ $\Delta H_{\text{f CO}_2}^\circ = -393.5 \text{ kJ/mol}$

When **1 mole** of a substance is formed from its elements in their **standard states**, then the enthalpy change for that reaction is called the **standard enthalpy of formation, $\Delta H_{\text{f}}^\circ$**

The **standard state** is the form of an element (solid, liquid, or gas, diatomic or monatomic etc.) found at 1 atm of pressure. Any temperature may be used although most data is collected at 25°C.

Know: the definition and conditions for enthalpies of combustion, fusion, vaporization and formation.

Substance	$\Delta H_{\text{f}}^\circ$ (kJ/mol)	Substance	$\Delta H_{\text{f}}^\circ$ (kJ/mol)
Ag(s)	0	H ₂ O ₂ (l)	-187.6
AgCl(s)	-127.0	Hg(l)	0
Al(s)	0	I ₂ (s)	0
Al ₂ O ₃ (s)	-1669.8	HI(g)	25.9
Br ₂ (l)	0	Mg(s)	0
HBr(g)	-36.2	MgO(s)	-601.8
C(graphite)	0	MgCO ₃ (s)	-1112.9
C(diamond)	1.90	N ₂ (g)	0
CO(g)	-110.5	NH ₃ (g)	-46.3
CO ₂ (g)	-393.5	NO(g)	90.4
Ca(s)	0	NO ₂ (g)	33.85
CaO(s)	-635.6	N ₂ O ₄ (g)	9.66
CaCO ₃ (s)	-1206.9	N ₂ O(g)	81.56
Cl ₂ (g)	0	O(g)	249.4
HCl(g)	-92.3	O ₂ (g)	0
Cu(s)	0	O ₃ (g)	142.2
CuO(s)	-155.2	S(rhombic)	0
F ₂ (g)	0	S(monoclinic)	0.30
HF(g)	-271.6	SO ₂ (g)	-296.1
H(g)	218.2	SO ₃ (g)	-395.2
H ₂ (g)	0	H ₂ S(g)	-20.15
H ₂ O(g)	-241.8	ZnO(s)	-348.0
H ₂ O(l)	-285.8		

What are the Standard States of the Elements at 25°C and 1 atm Pressure?

•Remember the diatomic elements: H₂, N₂, O₂, F₂, Cl₂, Br₂, and I₂

•All elements are Solids EXCEPT:

•Gases are: H₂, N₂, O₂, F₂, Cl₂, and the Noble Gases

•Liquids are: Br₂ and Hg

1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.91	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.20	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.20	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.03	89 Ac 227.03	104 Rf (261)	105 Ha (262)	[106] (263)	[107] (262)	[108] (265)	[109] (266)									

Lanthanide series

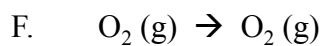
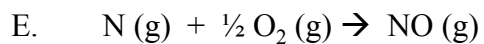
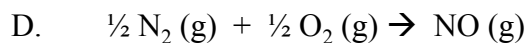
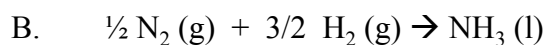
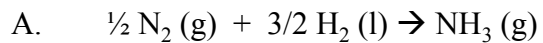
58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Actinide series

Formation Reactions

Clicker Questions:

For each of the following reactions, identify if the reaction is a formation reaction:

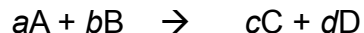


What is the ΔH of the last reaction (reaction F) above?

What is the heat of formation of an element in its standard state?

Using Enthalpies of Formation

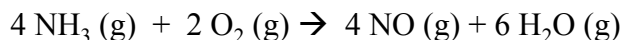
- We can use tabulated enthalpies of formation to calculate the ΔH of any reaction! What is the approach to doing this?



$$\Delta H_{\text{rxn}}^0 = [c\Delta H_f^0(\text{C}) + d\Delta H_f^0(\text{D})] - [a\Delta H_f^0(\text{A}) + b\Delta H_f^0(\text{B})]$$

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

Bonus: Using information on table 6.4, determine the ΔH for the following reaction?



Substance	ΔH_f^0 (kJ/mol)	Substance	ΔH_f^0 (kJ/mol)
Ag(s)	0	H ₂ O ₂ (l)	-187.6
AgCl(s)	-127.0	Hg(l)	0
Al(s)	0	I ₂ (s)	0
Al ₂ O ₃ (s)	-1669.8	HI(g)	25.9
Br ₂ (l)	0	Mg(s)	0
HBr(g)	-36.2	MgO(s)	-601.8
C(graphite)	0	MgCO ₃ (s)	-1112.9
C(diamond)	1.90	N ₂ (g)	0
CO(g)	-110.5	NH ₃ (g)	-46.3
CO ₂ (g)	-393.5	NO(g)	90.4
Ca(s)	0	NO ₂ (g)	33.85
CaO(s)	-635.6	N ₂ O ₄ (g)	9.66
CaCO ₃ (s)	-1206.9	N ₂ O(g)	81.56
Cl ₂ (g)	0	O(g)	249.4
HCl(g)	-92.3	O ₂ (g)	0
Cu(s)	0	O ₃ (g)	142.2
CuO(s)	-155.2	S(rhombic)	0
F ₂ (g)	0	S(monoclinic)	0.30
HF(g)	-271.6	SO ₂ (g)	-296.1
H(g)	218.2	SO ₃ (g)	-395.2
H ₂ (g)	0	H ₂ S(g)	-20.15
H ₂ O(g)	-241.8	ZnO(s)	-348.0
H ₂ O(l)	-285.8		

Putting it All Together: Thermochemistry

If 247 grams of ice at -15°C are added to 300 grams of hot tea at 90°C , what is the final temperature of this mixture?

Note the specific heat of tea is the same as for water.

Properties of water:

Specific heat of the solid = 2.09 J/gK

Normal Freezing Point = 0°C

$\Delta H_{\text{fus}} = 6.01 \text{ kJ/mol}$

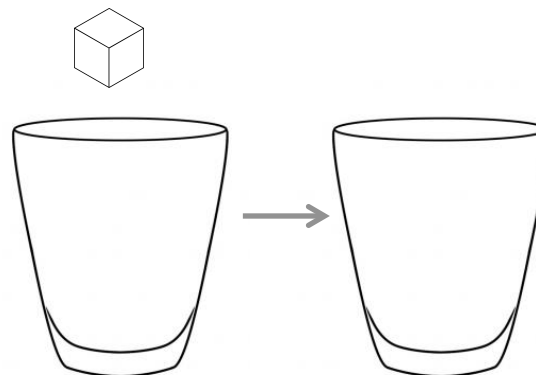
Specific heat of gas = 1.84 J/gK

Normal Boiling point = 100°C

$\Delta H_{\text{vap}} = 44 \text{ kJ/mol}$

Specific heat of liquid = 4.184 J/gK

a) Write the first law expression ($q + q + q \dots = 0$) for the tea and ice mixing:



Gas Laws, Work, Heat and Energy (Chang, *Essentials*, 6.77)

A 1.00-mole sample of ammonia at 14.0 atm and 25°C in a cylinder fitted with a movable piston expands against a constant external Pressure of 1.00 atm. At equilibrium, the pressure and volume of the gas are 1.00 atm and 23.5 L, respectively. Calculate the q , w and ΔE for the process. The specific heat of ammonia is 0.0258 J/g°C.

- a) Write the expressions for finding q and w for the process above. What do you know and what do you need to find?