

# Thermochemistry

CH 5

1

## Energy vocab

2

- ▶ Energy – capacity to do work or transfer heat
- ▶ Work – energy used to cause an object with mass to move against a force
- ▶ Heat – energy used to cause temperature to increase

## Energy vocab

3

- ▶ Kinetic energy – energy of motion
- ▶ Potential energy – stored energy or energy of position
- ▶ Energy units: Joules, cal, kJ, kcal (Cal)
- ▶  $4.184 \text{ J} = 1 \text{ cal}$

## Energy vocab

4

- ▶ Chemical energy – potential energy stored in arrangement of atoms in molecule
- ▶ Thermal energy – energy because of temperature

## Endothermic and exothermic processes

5

- ▶ Temperature changes indicate energy changes

## Endothermic and exothermic processes

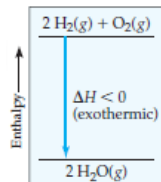
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- ▶ Endothermic processes
  - ▶ Products have higher energy than reactants
  - ▶ What does this feel like?

## Endothermic and exothermic processes

7

- ▶ Exothermic processes
- ▶ Reactants have higher energy than products
- ▶ What does this feel like?



## Exo- and endo- brainstorming

8

- ▶ List 5 everyday processes and label if they are endo- or exothermic
- ▶ How can you tell?
- ▶ Partner with someone at your table and double check their labels

## Endothermic and exothermic processes in chemistry systems

9

- ▶ Heating or cooling a substance
- ▶ Phase changes
  - ▶  $s \rightarrow l \rightarrow g$
  - ▶ Dissolution
- ▶ Chemical transformations

## Endothermic and exothermic processes in chemistry systems

10

- ▶ Heating or cooling a substance
  - ▶ Is heating a substance endo- or exo-?
  - ▶ Is cooling a substance endo- or exo-?

## Endothermic and exothermic processes in chemistry systems

11

- ▶ Phase changes
  - ▶  $s \rightarrow l \rightarrow g$ 
    - ▶ Adding heat rearranges IMFs ( $s \rightarrow l$ ) or overcomes attractions due to IMFs ( $l \rightarrow g$ )
  - ▶  $g \rightarrow l \rightarrow s$ 
    - ▶ What is happening with heat?

## Endothermic and exothermic processes in chemistry systems

12

- ▶ Phase changes
  - ▶ Dissolution
    - ▶ Endo- or exo- depends on strength of IMFs in solid and water separately and on interparticle interactions when dissolved

## Endothermic and exothermic processes in chemistry systems

13

- ▶ Chemical transformations
- ▶ Chemical reactions

## Endothermic and exothermic processes

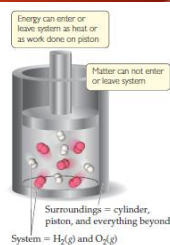
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- ▶ System – what we're studying
- ▶ Surroundings – everything else

## Endothermic and exothermic processes

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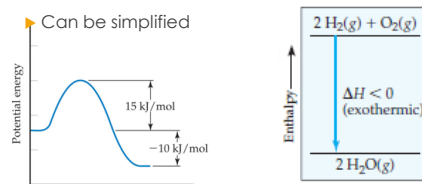
- ▶ Endothermic – system gains energy from surroundings
  - ▶ Work done ON system
- ▶ Exothermic – energy lost by system (reacting species) is gained by surroundings
  - ▶ Work done BY system



## Energy diagrams

16

▶ Can be simplified



## Heat transfer

17

- ▶ Particles of a warmer body have a higher average kinetic energy than particles of a cooler body
- ▶ Collisions can result in energy transfer (thermal contact)
  - ▶ Energy is transferred as heat

## Heat transfer

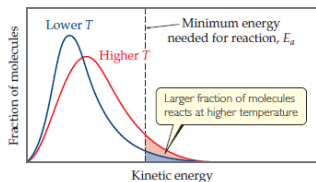
18

- ▶ Thermal equilibrium is reached when the average KE of particles is the same
  - ▶ Collisions still continue
  - ▶ Same average KE indicates same T

## Heat transfer

19

- ▶ Does thermal equilibrium mean no energy is transferred anymore?



## Heat capacity and calorimetry

20

- ▶ Energy transfer when cooler body is heated by warmer body
- ▶ Calorimetry experiments measure heat transfer
- ▶ Water and isopropanol demo

## Heat capacity and calorimetry

21

- ▶  $q = mC\Delta T$
- ▶  $q \equiv$  heat (J)
- ▶  $m \equiv$  mass (g)
- ▶  $C \equiv$  specific heat ( $J/g^\circ C$ )
- ▶  $\Delta T \equiv$  change in T,  $\Delta T = T_f - T_i$  ( $^\circ C$ )

Heat capacity and calorimetry  
Sample problem

22

How much heat is needed to warm 250 g of water from  $15^\circ C$  (the previous temperature in our classroom) to  $95^\circ C$  (the approximate boiling point in Denver)? **84 000 J**

Using the same amount of heat, what would be the final temperature of a 250 g piece of iron?  **$760^\circ C$**

Heat capacity and calorimetry  
Practice 1

23

1. The specific heat of graphite is  $0.71 J/g^\circ C$ . Calculate the energy needed to raise the temperature of 75 g of graphite from 294 K to 348 K. **2900 J**
2. Aluminum has a specific heat capacity of  $0.902 J/g^\circ C$ . How much energy is released when 1.0 kg of aluminum cools from  $35^\circ C$  to  $20^\circ C$ ? **-14 000 J**

## Heat capacity and calorimetry

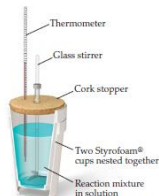
24

- ▶ First law of thermodynamics – energy is conserved in chemical and physical processes
- ▶ Examples?
- ▶ Transfer of specific amount of heat will not produce the same temperature change
- ▶ Due to different heat capacities

## Heat capacity and calorimetry (Constant pressure)

25

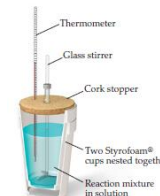
- ▶ Heat lost by reaction is gained by surroundings
- ▶ Heat gained by reaction is lost by surroundings
- ▶  $q_{\text{rxn}} = -q_{\text{surroundings}}$
- ▶  $q_{\text{rxn}} = -q_{\text{soln}}$



## Heat capacity and calorimetry Sample problem

26

- ▶ A 46.2 g sample of copper is heated to 95.4°C and then placed in a calorimeter containing 75.0 g of water at 19.6°C. The final temperature of both the water and the copper is 21.8°C. What is the specific heat of copper?  
**0.203 J/g °C**



## Heat capacity and calorimetry Practice 2

27

1. A piece of metal weighing 59.047 g was heated to 100.0 °C and then put it into 100.0 mL of water (initially at 23.7 °C). The metal and water were allowed to come to an equilibrium temperature, determined to be 27.8 °C. Assuming no heat lost to the environment, calculate the specific heat of the metal. **0.402 J/g °C**

## Heat capacity and calorimetry Practice 2

28

2. What is the final temperature when 0.032 kg of milk at 11 °C is added to 0.16 kg of coffee at 91 °C? Assume the specific heat capacities of the two liquids are the same as water, and disregard any energy transfer to the surroundings. **78 °C**

## Heat capacity and calorimetry

29

- ▶ Other terms
  - ▶ Heat capacity – heat (J) required to raise T by 1°C, not specific to mass
  - ▶ Molar heat capacity – heat capacity of 1 mol of substance

## Heat capacity and calorimetry Practice 3

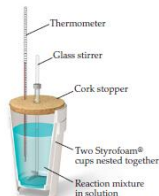
30

1. Determine the heat needed to increase the temperature of 10.0 g of mercury by 7.5°C. The molar heat capacity for mercury is 27.8 J/mol°C. **10. J**
2. The specific heat of iron is 0.451 J/g°C. What is the molar specific heat of iron? **25.2 J/mol °C**

### Heat capacity and calorimetry (Constant pressure)

31

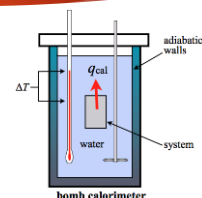
- ▶ Calorimeter also absorbs heat
- ▶ Add hot water to cold water in calorimeter
- ▶ Calculate  $q$  lost by hot water
- ▶ Calculate  $q$  gained by cold water
- ▶ Calorimeter gained the rest



### Heat capacity and calorimetry (Constant volume)

32

- ▶ Bomb calorimeter
- ▶ Known heat capacity (not specific heat),  $C_{\text{cal}}$
- ▶  $q = C_{\text{cal}}\Delta T$
- ▶ FOCUS ON UNITS!!!!

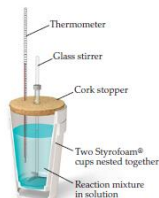


### Heat capacity and calorimetry Sample problem

33

When 40.0 mL of water at 60.0°C is added to 40.0 mL water at 25.0°C already in a calorimeter, the temperature rises 15.0°C. What is the heat capacity of the calorimeter?

**55.8 J/°C**



### Heat capacity and calorimetry Sample problem

34

- ▶ When 50.0 mL of 0.10 M HCl(aq) and 50.0 mL of 0.10 M NaOH(aq), both at 22.0 °C, are added to a coffee cup calorimeter, the temperature of the mixture reaches a maximum of 28.9 °C. What is the approximate amount of heat produced by this reaction? **2890 J**

### Heat capacity and calorimetry Practice 4

35

1. 50.0 mL of water at 40.5 °C is added to a calorimeter containing 50.0 mL of water at 17.4 °C. After waiting for the system to equilibrate, the final temperature reached is 28.3 °C. Calculate the heat capacity of the calorimeter (just the calorimeter without water). **25 J/°C**

### Heat capacity and calorimetry Practice 4

36

2. When 100. mL of 0.200 M NaCl(aq) and 100. mL of 0.200 M AgNO<sub>3</sub>(aq), both at 21.9 °C, are mixed in a coffee cup calorimeter, the temperature increases to 23.5 °C. Write a balanced equation and net ionic equation. How much heat is produced by this precipitation reaction? What assumptions did you make to determine your value? **1340 J**

## Heat capacity and calorimetry Practice 4

37

3. When 3.12 g of glucose,  $C_6H_{12}O_6$ , is burned in a bomb calorimeter, the temperature of the calorimeter increases from 23.8 °C to 35.6 °C. The calorimeter contains 775 g of water, and the bomb itself has a heat capacity of 893 J/°C. How much heat was produced by the combustion of the glucose sample? **-48.8 kJ**

## Changing energy

38

- ▶ Systems change energy through
  - ▶ Heating/cooling
  - ▶ Phase changes
  - ▶ Chemical reactions

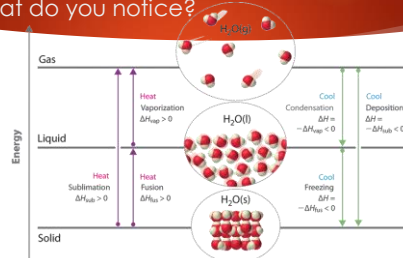
## Energy of phase changes

39

- ▶  $s \rightarrow l \rightarrow g$  Requires heat
  - ▶ Energy of system increases
- ▶  $g \rightarrow l \rightarrow s$  Releases heat
  - ▶ Energy of system decreases
- ▶ T of pure substance remains constant during phase change

## Energy of phase changes What do you notice?

40



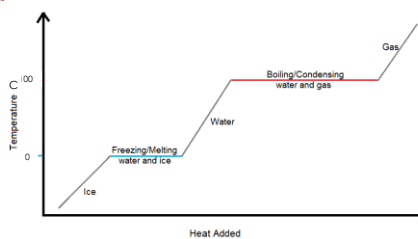
## Energy of phase changes

41

- ▶ How are  $\Delta H_{vap}$  and  $\Delta H_{condense}$  related?
- ▶ If  $\Delta H_{fus}$  of ethanol is 5.02 kJ/mol at its melting point, -114 °C. What is its  $\Delta H_{solid}$  at the same temperature?
- ▶ How much heat is required to melt 2.50 mol of ethanol at -114 °C?

## Energy of phase changes Heating curves

42



### Energy of phase changes Heating curves

43

- ▶ Label your heating curve
- ▶ What is happening from A to B? As you add heat, what are the particles doing? What is the heat being used for?
- ▶ B to C?
- ▶ C to D?
- ▶ D to E?
- ▶ E to F?

### Energy of phase changes

44

- ▶ Heating s, l, or g increases T, average KE
- ▶ During phase transitions  $\Delta T=0$  therefore ave KE doesn't change
  - ▶ PE changes, modifying/overcoming IMFs

### Energy of phase changes Practice 5

45

1. Calculate the heat required to change 9.00 g of solid  $\text{H}_2\text{O}$  at  $-25^\circ\text{C}$  to vapor at  $125^\circ\text{C}$ . The specific heats of ice, liquid water, and steam are  $2.03 \text{ J/g}\cdot\text{K}$ ,  $4.184 \text{ J/g}\cdot\text{K}$ , and  $1.84 \text{ J/g}\cdot\text{K}$ , respectively.  $\Delta H_{\text{fus}} = 6.01 \text{ kJ/mol}$  and  $\Delta H_{\text{vap}} = 40.67 \text{ kJ/mol}$ . **27.9 kJ**

### Energy of phase changes Practice 5

46

2. Calculate the heat released when 9.00 g of  $\text{H}_2\text{O}$  vapor at  $125^\circ\text{C}$  is cooled to a solid at  $-25^\circ\text{C}$ . The specific heats of ice, liquid water, and steam are  $2.03 \text{ J/g}\cdot\text{K}$ ,  $4.184 \text{ J/g}\cdot\text{K}$ , and  $1.84 \text{ J/g}\cdot\text{K}$ , respectively.  $\Delta H_{\text{solid}} = -6.01 \text{ kJ/mol}$  and  $\Delta H_{\text{condense}} = -40.67 \text{ kJ/mol}$ . **-27.9 kJ**

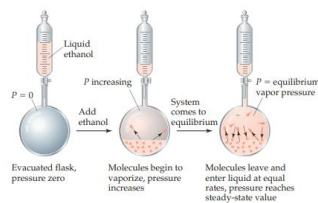
### Energy of phase changes Vapor pressure

47

- ▶ In a liquid, some molecules at surface escape to vapor.
- ▶ Molecules vaporize, then condense

### Energy of phase changes Vapor pressure

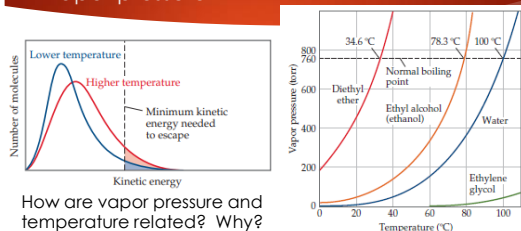
48





## Energy of phase changes Vapor pressure

49



How are vapor pressure and temperature related? Why?

## Introduction to enthalpy of reaction

50

- ▶ Enthalpy change of a reaction is the amount of heat energy released/absorbed at constant pressure
- ▶ At constant P,  $\Delta H = q$
- ▶ Heat = energy ( $q = E$ )  $\therefore \Delta H = \Delta E$

## Introduction to enthalpy of reaction Sample problems

51

- $\text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 890 \text{ kJ} \rightarrow \text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g})$   
How much heat is needed for 10.0 g of carbon dioxide to react?  $2.0 \times 10^2 \text{ kJ}$
- $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g}) \quad \Delta H = -890 \text{ kJ}$   
How much heat is released with 10.0 g of carbon dioxide is produced?  $-2.0 \times 10^2 \text{ kJ}$

## Introduction to enthalpy of reaction Practice 6

52

- $2 \text{H}_2\text{O}_2(\text{l}) \rightarrow 2 \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) + 196 \text{ kJ}$   
Calculate the quantity of heat released when 5.00 g of hydrogen peroxide decomposes.  $-14.4 \text{ kJ}$
- $\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g}) \quad \Delta H = -890 \text{ kJ}$   
How much heat is released with 4.50 g of methane gas is burned?  $-250. \text{ kJ}$

## Bond enthalpies

53

- ▶ Breaking and forming bonds changes the potential energy
- ▶ Energy required to break bonds
- ▶ Energy released by forming bonds

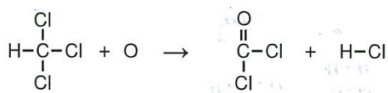
## Bond enthalpies

54

- ▶ Estimate energy needed to break bonds by adding up bond energies for all bonds broken
- ▶ Estimate energy released by forming bonds by adding up bond energies for all bonds formed
- ▶ Determine enthalpy for the reaction.

## Bond enthalpies Sample problem

55



## Bond enthalpies Activity

56

1. Correctly balanced equations
2. Build accurate models of reactants and products (showing single, double, triple bonds)
  - a. Keep in mind bond angles and length differences due to single, double, triple
3. Determine enthalpy change of the reaction

## Enthalpy of formation ( $\Delta H_f^\circ$ )

57

- ▶ Enthalpy change when forming a compound from its elements
- ▶  $_f$  indicates formation from elements
- ▶  $^\circ$  indicates standard state (1 atm, 25 °C/298 K)

## Enthalpy of formation ( $\Delta H_f^\circ$ )

58

- ▶ elements $^\circ$  → 1 mol compound
- ▶  $2 \text{ C (graphite)} + 3 \text{ H}_2(\text{g}) + 1/2 \text{ O}_2(\text{g}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{l})$
- ▶  $\Delta H_f^\circ = -277.7 \text{ kJ}$
- ▶  $\Delta H_f^\circ$  of most stable form of the element = 0 (like  $\text{H}_2$ ,  $\text{O}_2$ , C (graphite))

## Enthalpy of formation ( $\Delta H_f^\circ$ ) Practice 7

59

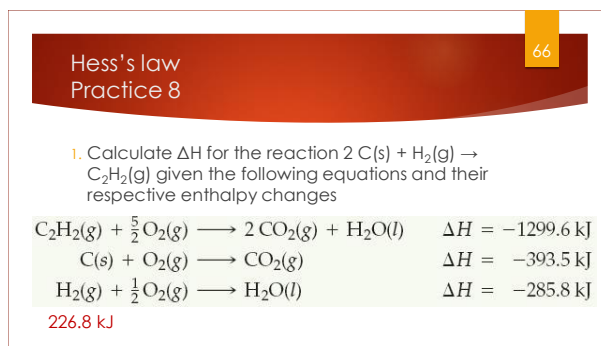
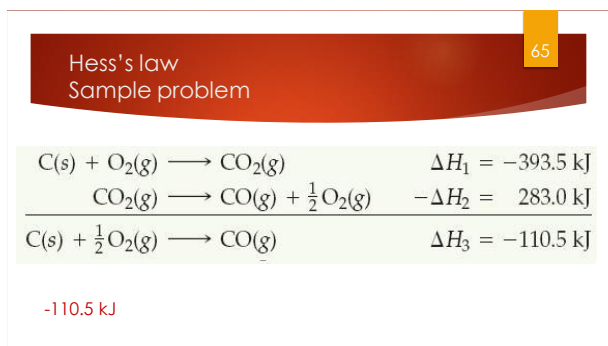
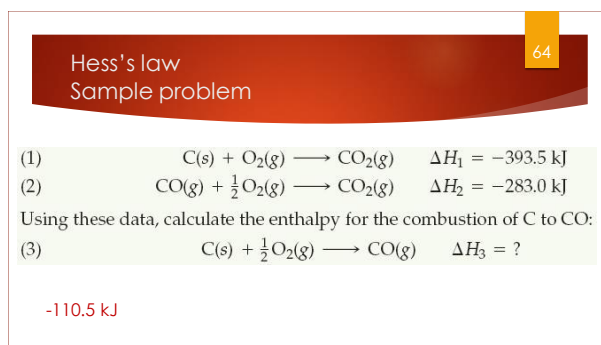
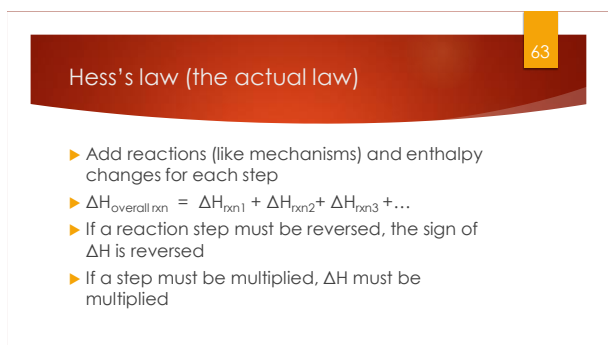
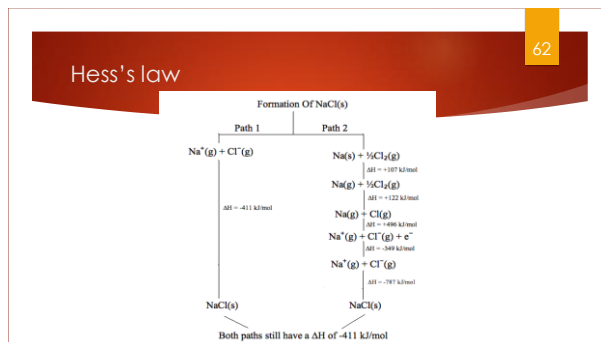
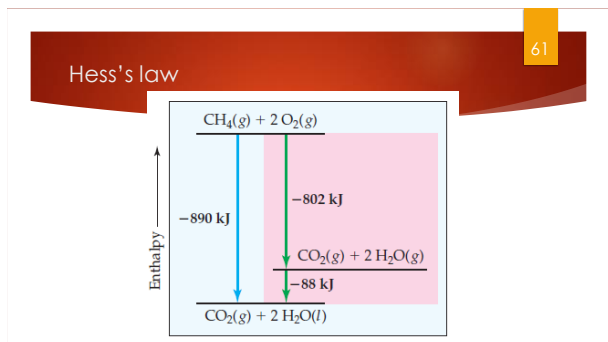
Write the equation for the formation of the following compounds from its elements in their standard states:

1. Sodium oxide
2. Potassium chloride
3. Glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ )

## Hess's law

60

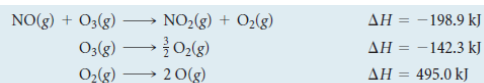
- ▶ Enthalpy is a state function
  - ▶ Only depends on initial and final states, not how you get there
  - ▶ Like displacement
  - ▶ Enthalpy depends on amount of matter that undergoes change, initial state of reactants, final state of products



Hess's law  
Practice 8

67

2. Calculate  $\Delta H$  for the reaction  $\text{NO(g)} + \text{O(g)} \rightarrow \text{NO}_2\text{(g)}$  given the following equations and their respective enthalpy changes

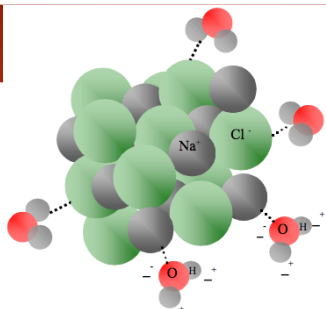


-304.1 kJ

## Hess's law

68

- ▶ Enthalpy of solution ( $\Delta H_{\text{soln}}$ ) released/absorbed when a solution is formed
- ▶ Breaking ionic bonds between solute molecules
- ▶ "Breaking" intermolecular attractions between solvent molecules
- ▶ Forming new solute-solvent attractive bonds
- ▶ Endo- or exo- depends on relative amounts of energy

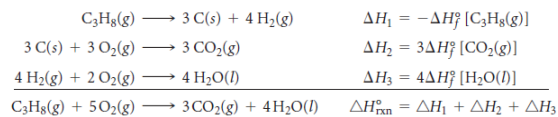


69

## Hess's law

70

- ▶ Use  $\Delta H_f^\circ$  to determine  $\Delta H_{\text{rxn}}^\circ$



## Hess's law

71

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

- ▶ m and n mean USE STOICH

Hess's law  
Sample problem

72

- ▶ Calculate the standard enthalpy change for the combustion of 1 mole of benzene,  $\text{C}_6\text{H}_6\text{(l)}$  to its products ( $\text{H}_2\text{O}$  is liquid). **-3267.0 kJ**

TABLE 6.3 • Standard Enthalpies of Formation,  $\Delta H_f^\circ$ , at 298 K

Substance	Formula	$\Delta H_f^\circ$ (kJ/mol)	Substance	Formula	$\Delta H_f^\circ$ (kJ/mol)
Acetylene	$C_2H_2(g)$	226.7	Hydrogen chloride	$HCl(g)$	-92.30
Ammonia	$NH_3(g)$	-46.19	Hydrogen fluoride	$HF(g)$	-268.60
Benzene	$C_6H_6(l)$	49.0	Hydrogen iodide	$HI(g)$	25.9
Calcium carbonate	$CaCO_3(s)$	-1207.1	Methane	$CH_4(g)$	-74.80
Calcium oxide	$CaO(s)$	-635.5	Methanol	$CH_3OH(l)$	-238.6
Carbon dioxide	$CO_2(g)$	-393.5	Propane	$C_3H_8(g)$	-103.85
Carbon monoxide	$CO(g)$	-110.5	Silver chloride	$AgCl(s)$	-127.0
Diamond	$C(s)$	1.88	Sodium bicarbonate	$NaHCO_3(s)$	-947.7
Ethane	$C_2H_6(g)$	-84.68	Sodium carbonate	$Na_2CO_3(s)$	-1130.9
Ethanol	$C_2H_5OH(l)$	-277.7	Sodium chloride	$NaCl(s)$	-410.9
Ethylene	$C_2H_4(g)$	52.30	Sucrose	$C_{12}H_{22}O_{11}(s)$	-2221
Glucose	$C_6H_{12}O_6(s)$	-1273	Water	$H_2O(l)$	-285.8
Hydrogen bromide	$HBr(g)$	-36.23	Water vapor	$H_2O(g)$	-241.8

Substance	Formula	$\Delta H_f^\circ$ (kJ/mol)
Acetylene	$C_2H_2(g)$	226.7
Ammonia	$NH_3(g)$	-46.19
Benzene	$C_6H_6(l)$	49.0
Calcium carbonate	$CaCO_3(s)$	-1207.1
Calcium oxide	$CaO(s)$	-635.5
Carbon dioxide	$CO_2(g)$	-393.5
Carbon monoxide	$CO(g)$	-110.5
Diamond	$C(s)$	1.88
Ethane	$C_2H_6(g)$	-84.68
Ethanol	$C_2H_5OH(l)$	-277.7
Ethylene	$C_2H_4(g)$	52.30
Glucose	$C_6H_{12}O_6(s)$	-1273
Hydrogen bromide	$HBr(g)$	-36.23

Substance	Formula	$\Delta H_f^\circ$ (kJ/mol)
Hydrogen chloride	$HCl(g)$	-92.30
Hydrogen fluoride	$HF(g)$	-268.60
Hydrogen iodide	$HI(g)$	25.9
Methane	$CH_4(g)$	-74.80
Methanol	$CH_3OH(l)$	-238.6
Propane	$C_3H_8(g)$	-103.85
Silver chloride	$AgCl(s)$	-127.0
Sodium bicarbonate	$NaHCO_3(s)$	-947.7
Sodium carbonate	$Na_2CO_3(s)$	-1130.9
Sodium chloride	$NaCl(s)$	-410.9
Sucrose	$C_{12}H_{22}O_{11}(s)$	-2221
Water	$H_2O(l)$	-285.8
Water vapor	$H_2O(g)$	-241.8

## Hess's Law Practice 9

1. Calculate the enthalpy change for the decomposition of calcium carbonate into calcium oxide and carbon dioxide. **178.1 kJ/mol**
2. Calculate the enthalpy change for the combustion of 1 mol of  $C_2H_5OH$  (the water is liquid). **-1366.7 kJ/mol**
3. Calculate the standard enthalpy of formation of  $CuO(s)$ .

## Hess's Law

- What happens if the products of a reaction are at a different temperature from the surroundings?