

# **Grade 12 Chemistry**

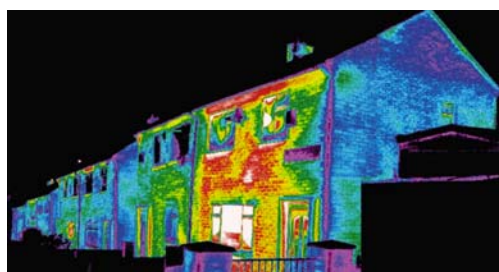
Energy Changes and Rates of Reaction  
Class 8

## **Overall Expectations**

- Analyze technologies and chemical processes that are based on energy changes, and evaluate them in terms of their efficiency and their effects on the environment
- Investigate and analyze energy changes and rates of reaction in physical and chemical processes, and solve related problems
- Demonstrate an understanding of energy changes and rates of reaction

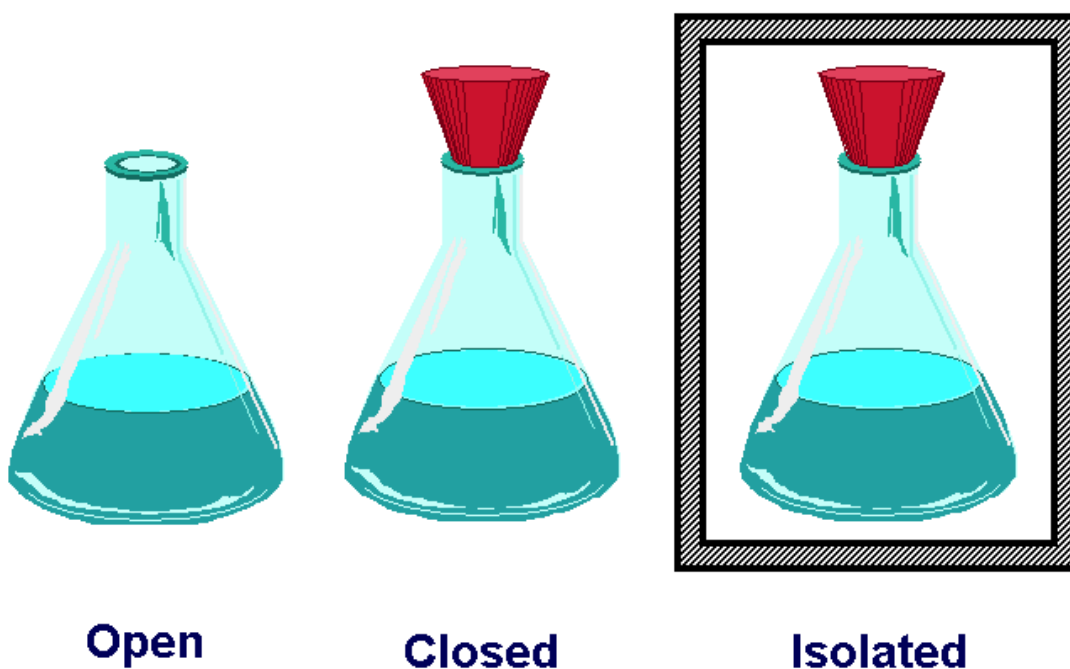
# Energy Changes in Chemical Reactions

- **Heat** – the transfer of thermal energy between two bodies that are at different temperatures
- **Thermochemistry** – the study of heat change in chemical reactions



- **System** – the specific part of the universe that is of interest to us
  - Ex: Chemical reaction, experiment, etc.
  - Three Types:
    - 1) Open System – can exchange mass and energy with its surroundings
    - 2) Closed System – allows the transfer of energy but not mass
    - 3) Isolated System – does not allow the transfer of energy or mass
- **Surroundings** – the rest of the universe outside of the system

## System



(c) C. Rose-Patrick, Brown University, 7-Jan-99, Chem 201 #1

## First Law of Thermodynamics

Energy can be converted from one form to another but cannot be created or destroyed  
(Law of Conservation of Energy)

$$\Delta E_{sys} + \Delta E_{surr} = 0$$

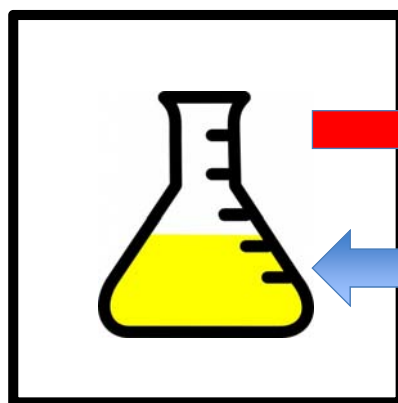
$$\Delta E_{sys} = -\Delta E_{surr}$$

Where  $\Delta E$  is the change in energy given by

$$\Delta E = E_f - E_i$$

**Surrounding:** the flask, the room, the universe

**System:** the reaction mixture being studied; the reactants and products



Energy out of system to surroundings: (-) sign

Energy into system from surroundings: (+) sign

- Energy changes are measured from the point of view of the system
- **Exothermic Process** – system gives off heat to the surrounding; (-) value
- **Endothermic Process** – system gains heat from the surroundings; (+) value

$$\Delta E = q + w$$

Where:

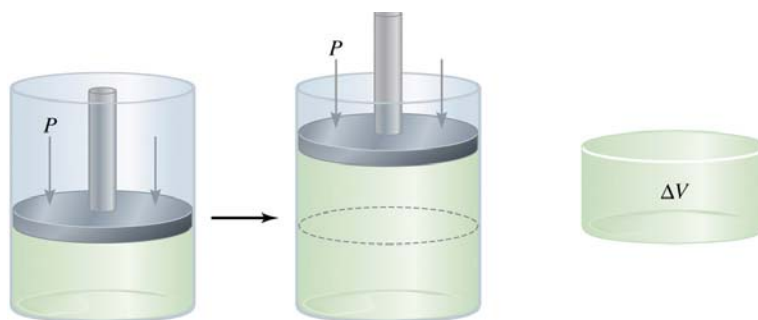
$q$  = the heat exchanged between the system and the surroundings

- $+q$  for an endothermic process
- $-q$  for an exothermic process

$w$  = work done on or by the system

- $+w$  for work done on the system by the surroundings
- $-w$  for work done by the system on the surroundings

## Work



Where:

$$w = -P\Delta V$$

P is the external atmospheric pressure

$\Delta V$  is the change in volume  $V_f - V_i$

Units:  $1\text{L}\cdot\text{atm} = 101.3\text{J}$



## Checkpoint



The work done when a gas is compressed in a cylinder is 462 J. During this process, there is a heat transfer of 128 J from the gas to the surroundings. Calculate the energy change for this process.

# Enthalpy of Chemical Reactions

- If a chemical reaction is run at *constant volume* then  $\Delta V=0$  and no P-V work will result

$$\Delta E = q - P\Delta V$$

$$\Delta E = q_v$$

- Where  $q_v$  refers to heat at constant volume

- If a chemical reaction is run at constant pressure

$$\Delta E = q + w$$

$$\Delta E = q_p - P\Delta V$$

$$q_p = \Delta E + P\Delta V$$

- Where  $q_p$  denotes heat at constant pressure

- **Enthalpy (H)** – the total energy of a substance at a constant pressure; heat change at constant pressure

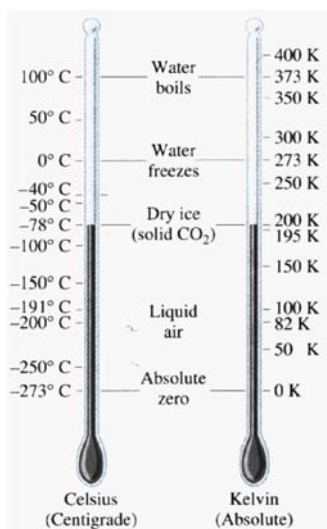
$$q_p = \Delta E + P\Delta V$$

$$H = E + PV$$

$$\Delta H = \Delta E + P\Delta V$$

- Chemists do not study the absolute enthalpy but rather the enthalpy change  $\Delta H$  of the reaction

## Heat and Temperature



- Heat (q) refers to the transfer of kinetic energy; expressed in joules (J)
  - Heat transfers from a warmer object to a cooler object
- Temperature (T) measures average kinetic energy of the substance in the system
  - Measured in Celsius (a relative scale)
  - Measured in Kelvins (an absolute scale)
    - Kelvins = Celsius + 273.15

## What is the difference between Heat and Enthalpy?

- Heat (q) – transfer of kinetic energy; expressed in joules (J)
- Enthalpy (H) – Total energy of a substance at *constant pressure* in a system; expressed in joules (J)
- Temperature (T) – measure of the average kinetic energy of the particles in the substance or system; expressed in kelvins (K)

## Enthalpy of Reactions $\Delta H_{\text{rxn}}$

- The difference between the enthalpies of the products and the reactants

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

- Endothermic Process =  $\Delta H > 0$  (positive)
- Exothermic Process =  $\Delta H < 0$  (negative)
- Enthalpy is a *state function* – independent of pathway



Table 1: Summary of differences between state and path functions

State Function	Path Function
Independent of path taken to establish property or value.	Dependent on path taken to establish property or value.
Can integrate using final and initial values.	Need multiple integrals and limits of integration in order to integrate.
Multiple steps result in same value.	Multiple steps result in different value.
Based on established state of system (temperature, pressure, amount, and identity of system).	Based on how state of system was established.

At 0°C and 1 atm, ice melts to form liquid water. Every mole of ice converted to liquid water under these conditions requires 6.01 kJ of heat energy to be absorbed



- The  $\Delta H$  value refers to all the reacting species in molar quantities
- Expressing  $\Delta H$  in kJ/mol rather than kJ conforms to the standard convention

## Enthalpy Guidelines:

1. Must specify the physical states of all reactants and products
2. If reactants and products are multiplied by a factor  $n$ , then  $\Delta H$  must also be multiplied by a factor  $n$



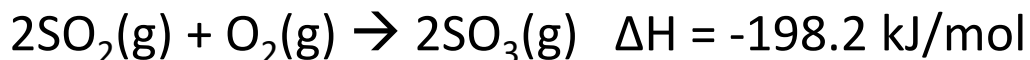
3. If we reverse the equation, the sign of  $\Delta H$  must change



## Checkpoint

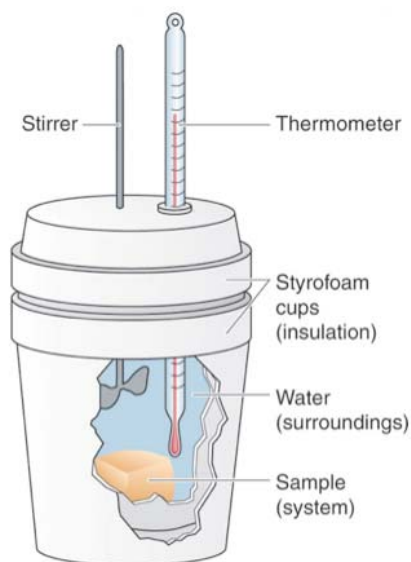


Given the thermochemical equation:



Calculate the heat evolved when 87.9g of  $\text{SO}_2$  (molar mass = 64.07g/mol) is converted.

# Calorimetry



- Calorimeter – a closed container designed to measure heat changes
- Calorimetry – the measurement of heat changes

## Specific Heat and Heat Capacity

- Specific Heat ( $c$ ) of a substance is the amount of heat required to raise the temperature of *one gram* of the substance by one degree Celsius;  $\text{J/g}\cdot^{\circ}\text{C}$
- Heat Capacity ( $C$ ) is the amount of heat required to raise the temperature of *a given quantity* of the substance by one degree Celsius;  $\text{J}/^{\circ}\text{C}$

**Table 5.2** Specific Heat Capacities of Selected Substances

Substance	Specific heat capacity (J/g • °C at 25°C)
Element	
aluminum	0.900
carbon (graphite)	0.711
hydrogen	14.267
iron	0.444
Compound	
ammonia (liquid)	4.70
ethanol	2.46
ethylene glycol	2.42
water (liquid)	4.184
Other material	
air	1.02
concrete	0.88
glass	0.84
wood	1.76

- Ex: The specific heat of water is 4.184 J/g•°C and the heat capacity of 60.0g of water is

$$(60.0\text{g})(4.184 \text{ J/g}\cdot^{\circ}\text{C}) = 251 \text{ J}/^{\circ}\text{C}$$

$$q = mc\Delta T$$

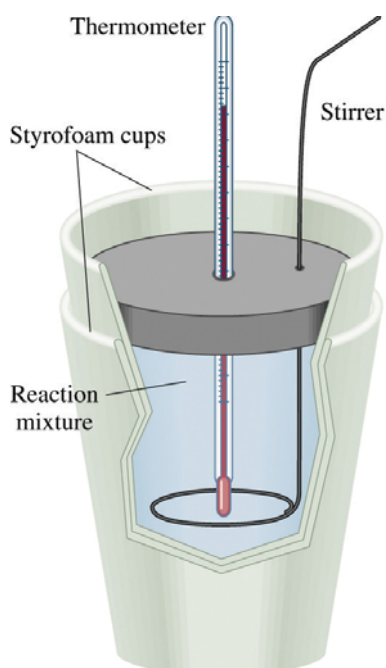


## Checkpoint



When 600 ml of water in an electric kettle is heated from 20°C to 85°C to make a cup of tea, how much heat flows into the water?

## Constant-Pressure Calorimetry



- Aka: Coffee-Cup Calorimeter
- Used to determine heat change in non-combustion reactions (i.e. acid-base neutralization, heat of solution and dilution)

# Assumptions for Calorimetry

1. No heat is transferred between the calorimeter and the outside environment
2. Any heat absorbed or released by the calorimeter (such as the container) is negligible
3. When a dilute aqueous solution is used in a calorimeter, you can assume that the solution has the same density and heat capacity as pure water ( $d=1.00$ ;  $C=4.184\text{J/g}^\circ\text{C}$ )



## Checkpoint



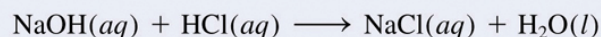
A lead (Pb) pellet having a mass of 26.47 g at  $89.98^\circ\text{C}$  was placed in a constant-pressure calorimeter of negligible heat capacity containing 100.0 mL of water. The water temperature rose from  $22.50^\circ\text{C}$  to  $23.17^\circ\text{C}$ . What is the specific heat of the lead pellet?



## Checkpoint



A quantity of  $1.00 \times 10^2$  mL of  $0.500\text{ M}$  HCl was mixed with  $1.00 \times 10^2$  mL of  $0.500\text{ M}$  NaOH in a constant-pressure calorimeter of negligible heat capacity. The initial temperature of the HCl and NaOH solutions was the same,  $22.50^\circ\text{C}$ , and the final temperature of the mixed solution was  $25.86^\circ\text{C}$ . Calculate the heat change for the neutralization reaction on a molar basis



Assume that the densities and specific heats of the solutions are the same as for water ( $1.00\text{ g/mL}$  and  $4.184\text{ J/g}\cdot^\circ\text{C}$ , respectively).



## Checkpoint



When  $0.7521\text{g}$  of benzoic acid was burned in a calorimeter containing  $1000\text{g}$  of water, a temperature rise of  $3.60^\circ\text{C}$  was observed. What is the heat capacity of the bomb calorimeter excluding the water? The heat of combustion of benzoic acid is  $-26.42\text{ kJ/g}$ .

## Enthalpy Changes $\Delta H_{\text{rxn}}$

- Enthalpy change for a reaction is  $\Delta H_{\text{rxn}}$  and is dependent on temperature and pressure
- Chemists often use  $\Delta H^{\circ}_{\text{rxn}}$  = the standard enthalpy of reaction at standard conditions (25°C and 1atm)
- Besides calorimetry there are three ways to calculate  $\Delta H^{\circ}_{\text{rxn}}$ :
  1. Hess's Law of Heat Summation
  2. Heat of Formation
  3. Bond Dissociation Energy

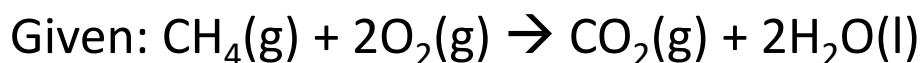
## Hess' Law of Summation

- Hess' Law – the overall enthalpy change for a reaction is equal to the sum of the enthalpy changes for the individual steps in the reaction
- Ex: 
$$\begin{array}{lcl} \text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} & \Delta H^{\circ}_1 = -394\text{kJ} & \\ \text{CO}_2\text{(g)} \rightarrow \text{CO(g)} + \frac{1}{2}\text{O}_2\text{(g)} & \Delta H^{\circ}_2 = +283\text{kJ} & \\ \hline \text{C(s)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO(g)} & \Delta H^{\circ}_{\text{rxn}} = -111\text{kJ} & \end{array}$$
- If the reaction is reversed, the sign of  $\Delta H$  is reversed too
- If an equation is multiplied by a constant, then  $\Delta H$  must be multiplied by that same constant

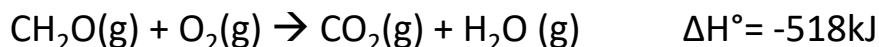
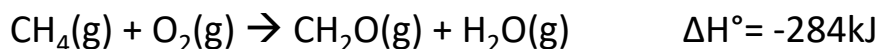




## Checkpoint



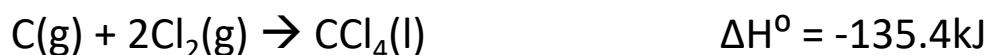
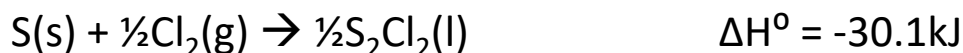
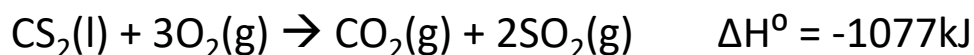
Use the following information to calculate  $\Delta H^\circ_{\text{rxn}}$  for the combustion of methane:



## Checkpoint



Carbon tetrachloride  $\text{CCl}_4$ , an organic solvent is prepared by the reaction of  $\text{Cl}_2$  with  $\text{CS}_2$ . Determine the heat of reaction for the reaction, given the following:



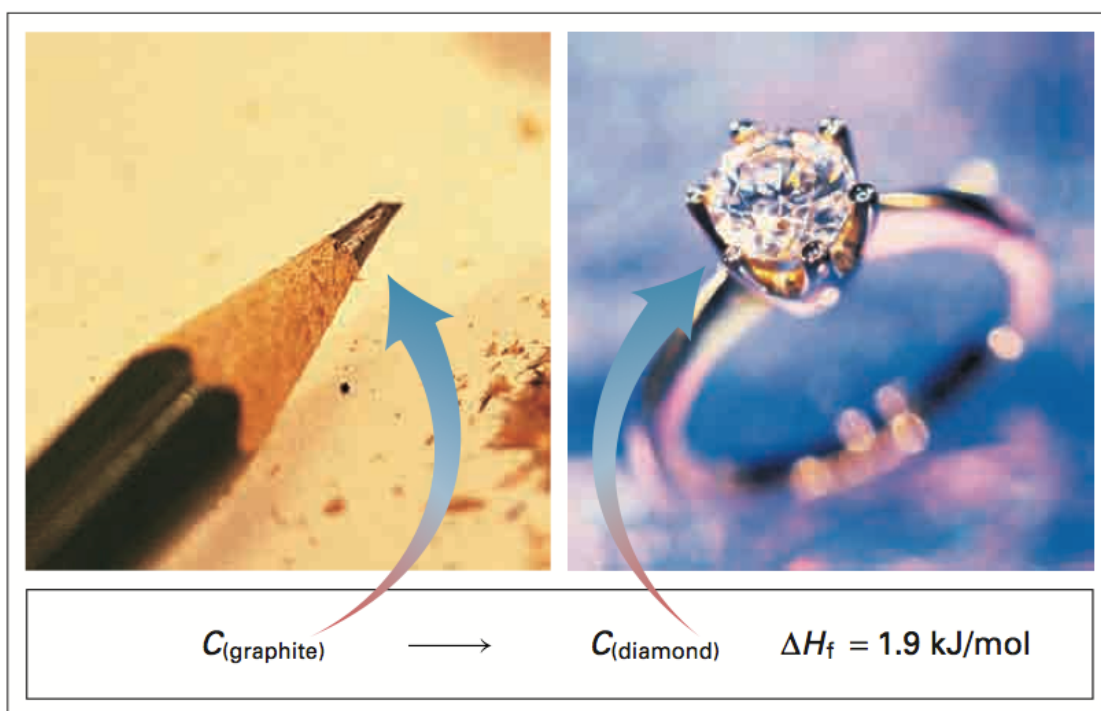
# Heat of Formation $\Delta H^\circ_f$

- $\Delta H^\circ_f$  is the enthalpy change for the formation of 1 mol of substance in its standard state from its constituent elements in their standard states

$$\Delta H^\circ_{\text{rxn}} = \Sigma(n\Delta H^\circ_f \text{ products}) - \Sigma(n\Delta H^\circ_f \text{ reactants})$$

where n=molar coefficients

- Elements in their standard state has  $\Delta H^\circ_f$  of zero;  
ex:  $\text{O}_2$   $\Delta H^\circ_f = 0$  kJ/mol while  $\text{O}_3$   $\Delta H^\circ_f = 143$  kJ/mol

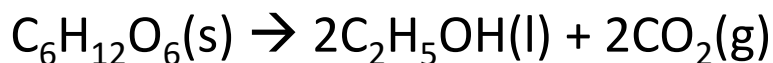


**Table 5.3** Selected Standard Molar Enthalpies of Formation

Compound	$\Delta H_f^\circ$	Formation equations
$\text{CO}_{(\text{g})}$	-110.5	$\text{C}_{(\text{s})} + \frac{1}{2}\text{O}_{2(\text{g})} \rightarrow \text{CO}_{(\text{g})}$
$\text{CO}_{2(\text{g})}$	-393.5	$\text{C}_{(\text{s})} + \text{O}_{2(\text{g})} \rightarrow \text{CO}_{2(\text{g})}$
$\text{CH}_{4(\text{g})}$	-74.6	$\text{C}_{(\text{s})} + 2\text{H}_{2(\text{g})} \rightarrow \text{CH}_{4(\text{g})}$
$\text{CH}_3\text{OH}_{(\ell)}$	-238.6	$\text{C}_{(\text{s})} + 2\text{H}_{2(\text{g})} + \frac{1}{2}\text{O}_{2(\text{g})} \rightarrow \text{CH}_3\text{OH}_{(\ell)}$
$\text{C}_2\text{H}_5\text{OH}_{(\ell)}$	-277.6	$2\text{C}_{(\text{s})} + 3\text{H}_{2(\text{g})} + \frac{1}{2}\text{O}_{2(\text{g})} \rightarrow \text{C}_2\text{H}_5\text{OH}_{(\ell)}$
$\text{C}_6\text{H}_{6(\ell)}$	+49.0	$6\text{C}_{(\text{s})} + 3\text{H}_{2(\text{g})} \rightarrow \text{C}_6\text{H}_{6(\ell)}$
$\text{C}_6\text{H}_{12}\text{O}_{6(\text{s})}$	-1274.5	$6\text{C}_{(\text{s})} + 6\text{H}_{2(\text{g})} + 3\text{O}_{2(\text{g})} \rightarrow \text{C}_6\text{H}_{12}\text{O}_{6(\text{s})}$
$\text{H}_2\text{O}_{(\ell)}$	-285.8	$\text{H}_{2(\text{s})} + \frac{1}{2}\text{O}_{2(\text{g})} \rightarrow \text{H}_2\text{O}_{(\ell)}$
$\text{H}_2\text{O}_{(\text{g})}$	-241.8	$\text{H}_{2(\text{s})} + \frac{1}{2}\text{O}_{2(\text{g})} \rightarrow \text{H}_2\text{O}_{(\text{g})}$
$\text{CaCl}_{2(\text{s})}$	-795.4	$\text{Ca}_{(\text{s})} + \text{Cl}_{2(\text{g})} \rightarrow \text{CaCl}_{2(\text{s})}$
$\text{CaCO}_{3(\text{s})}$	-1206.9	$\text{Ca}_{(\text{s})} + \text{C}_{(\text{s})} + \frac{3}{2}\text{O}_{2(\text{g})} \rightarrow \text{CaCO}_{3(\text{s})}$
$\text{NaCl}_{(\text{s})}$	-411.1	$\text{Na}_{(\text{s})} + \frac{1}{2}\text{Cl}_{2(\text{g})} \rightarrow \text{NaCl}_{(\text{g})}$
$\text{HCl}_{(\text{g})}$	-92.3	$\frac{1}{2}\text{H}_{2(\text{s})} + \frac{1}{2}\text{Cl}_{2(\text{g})} \rightarrow \text{HCl}_{(\text{g})}$
$\text{HCl}_{(\text{aq})}$	-167.5	$\frac{1}{2}\text{H}_{2(\text{s})} + \frac{1}{2}\text{Cl}_{2(\text{g})} \rightarrow \text{HCl}_{(\text{ag})}$



## Checkpoint



Use the following information to calculate  $\Delta H^\circ_{\text{rxn}}$  for the fermentation of glucose.

$$\Delta H_f^\circ [\text{C}_6\text{H}_{12}\text{O}_6(\text{s})] = -1260 \text{ kJ/mol}$$

$$\Delta H_f^\circ [\text{C}_2\text{H}_5\text{OH}(\text{l})] = -277.7 \text{ kJ/mol}$$

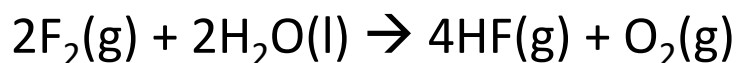
$$\Delta H_f^\circ [\text{CO}_2(\text{g})] = -393.5 \text{ kJ/mol}$$



## Checkpoint



Using the standard heats of formation,  $\Delta H^\circ_f$ , calculate the  $\Delta H^\circ_{rxn}$  of the following reaction:



## Bond Dissociation Energy (D)

- Only a few thousand  $\Delta H^\circ_f$  are known
- For the rest of the reactions, use bond dissociation energy since enthalpy is the energy stored in chemical bonds of a compound

$$\Delta H^\circ_{rxn} = D (\text{Reactant bonds}) - D (\text{Product bonds})$$

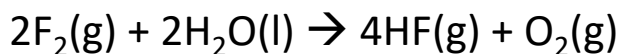
- D does not account for bond strength and polarity; values are only averages



## Checkpoint



Calculate the average bond energy (in kJ/mol) for an HF bond, given the following bond energies:

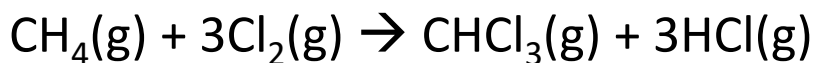


Bond		Bond Energy	
H-H	436kJ	O-O	142kJ
O-H	460kJ	O=O	499kJ
F-F	156kJ	H-F	565kJ

How were your answers different from the previous checkpoint?



## Checkpoint



Use the following information to calculate  $\Delta H^\circ_{\text{rxn}}$  synthesis of chloroform

C-H     $D = 410 \text{ kJ/mol}$

C-Cl     $D = 330 \text{ kJ/mol}$

Cl-Cl     $D = 243 \text{ kJ/mol}$

H-Cl     $D = 432 \text{ kJ/mol}$

# Cold Packs and Hot Packs

- $\Delta H_{\text{soln}}$  is called the enthalpy of solution or the enthalpy change when a solute dissolves in a solvent
- The pack usually has two separate chemicals with two separate compartments, once crushed or shaken, the compartment breaks and the chemicals mix
  - If reaction is endothermic, heat is absorbed from the surroundings = cold pack
  - If reaction is exothermic, heat is released to the surroundings = hot pack

