# Chem 123 (section 201)
# Lecture 4 (Jan. 12)

# Chapter 4 and Chapter 5

(p61-81)

**Learning Objectives**

By the end of this section, successful learners will be able to:

- Relate heat flow to change in temperature
- Define heat capacity
- Apply Hess's law to determine the enthalpy change of a reaction

Define standard enthalpy of formation and and identify the value for reference forms.

- The change of internal energy under constant volume condition equals to the heat exchange between the system and its surroundings! $\Delta E = q_V$
- The change of enthalpy under constant pressure condition equals to the heat exchange between the system and its surroundings! $\Delta H = q_p$

# Measurement of Heat: Calorimetry

## Heat capacity *C*

***Heat flows from hotter objects to colder objects***

$q = C\,\Delta T$, where $C$ is the heat capacity of the substance.

$C = q/\Delta T$ **(J K$^{-1}$)**

**The heat capacity is the energy needed to raise the temperature of the substance by 1 degree.**

The heat capacity generally depends on whether the volume or the pressure is kept constant.

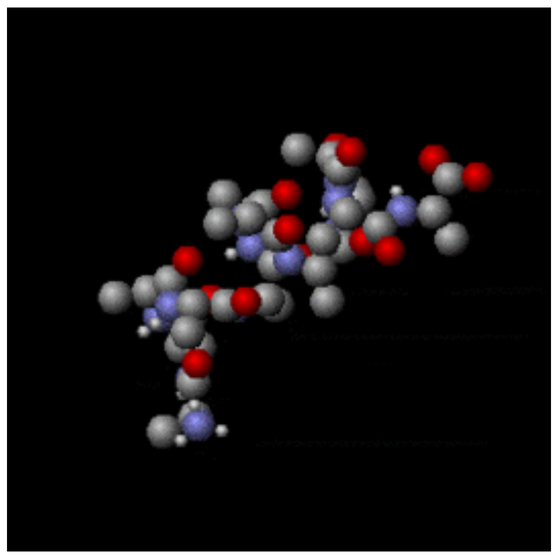
# Clicker question 1

Heat capacity is an extensive property

A) True

B) False

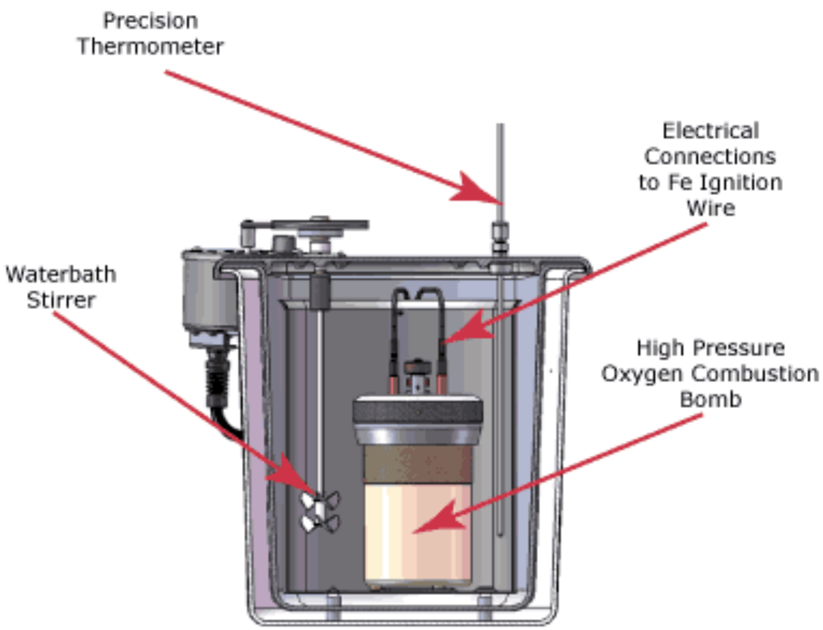
- Molar heat capacity $C_m$ *or* $\bar{C}$
- $\bar{C} = C/n$ $(J\ K^{-1}\ mol^{-1})$
- $\bar{C}$ is an intensive property. Unique to each substance



# Constant Volume: Bomb calorimeter

$$\Delta E = q_V$$

$$\Delta E = q_V = C_v \Delta T = n\overline{C}_v \Delta T$$

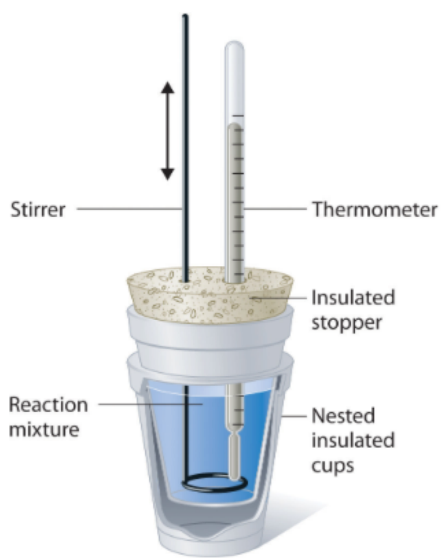



Parr Model 1341 Oxygen Bomb Calorimeter

# Constant Pressure: Coffee cup calorimeter

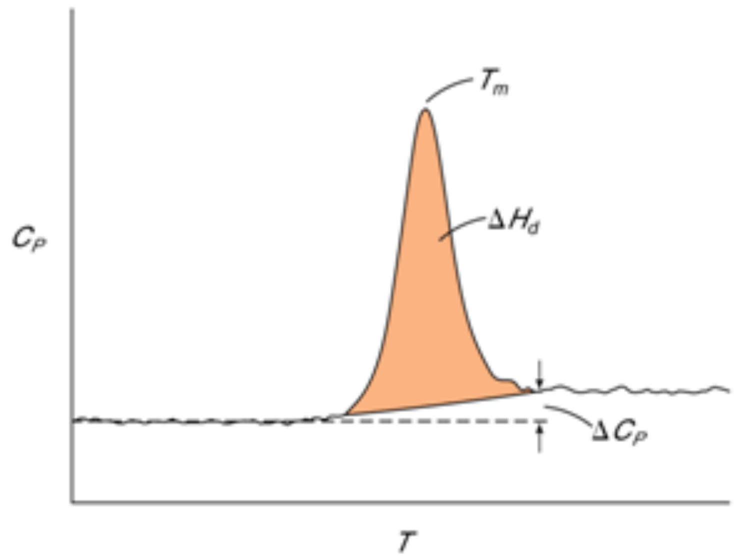
$$\Delta H = q_p$$

$$\Delta H = q_p = C_p \Delta T = n\overline{C}_P \Delta T$$




*Perkin Elmer DSC7 Differential Scanning Calorimeter*

# Applications in chemistry, life science and much much more…




**Chemical reaction, protein folding/unfolding, ligand binding…**

# Enthalpy change in chemical reactions

- Chemical reaction almost always involves changes in heat.
- Heat of reaction ($q_P$)is defined as the heat change in the transformation of reactants at some temperature and pressure to products at the same temperature and pressure.
- For a constant pressure process,
- $\Delta H = q_p$

# How to measure ΔH for chemical reactions?

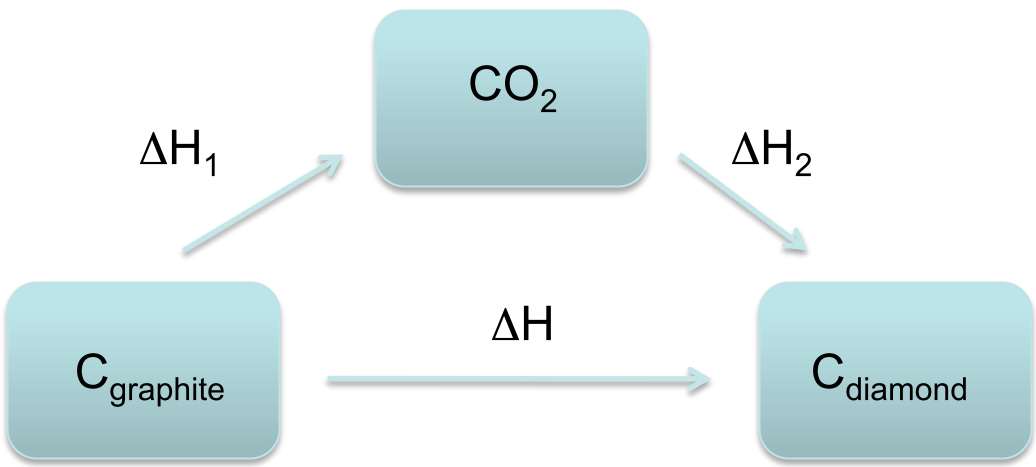
$$C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)} \quad \Delta H = ???$$

$$C_{graphite} \rightarrow C_{diamond} \quad \Delta H = ???$$

# Hess's Law

Sum of ΔH of all steps gives overall reaction enthalpy

H is a state function




$$\Delta H = \Delta H_1 + \Delta H_2$$

$$C_{graphite} + O_2\ (g) \rightarrow CO_2\ (g) \qquad \Delta H_1 = -393.5\ kJ$$

$$+\quad CO_2\ (g) \rightarrow C_{diamond} + O_2\ (g) \qquad \Delta H_2 = ???$$

---

$$C_{graphite} \rightarrow C_{diamond}$$

$C_{diamond} + O_2\ (g) \rightarrow CO_2\ (g)$ $\Delta H = -395.4\ kJ$

↓ ↓

$CO_2\ (g) \rightarrow C_{diamond} + O_2\ (g)$ $\Delta H = +395.4\ kJ$

$$C_{graphite} + O_2\ (g) \rightarrow CO_2\ (g) \qquad \Delta H_1 = -393.5\ kJ$$

$$+\ CO_2\ (g) \rightarrow C_{diamond} + O_2\ (g) \qquad \Delta H_2 = +395.4\ kJ$$

---

$$C_{graphite} \rightarrow C_{diamond} \qquad \Delta H = \Delta H_1 + \Delta H_2 = 1.9\ kJ$$

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H = -393.1 \text{ kJ}$$

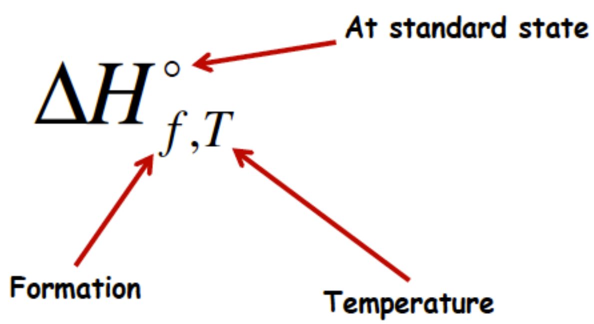
$$+ \quad CO_{2(g)} \rightarrow CO_{(g)} + \tfrac{1}{2}O_{2(g)} \qquad \Delta H = +282.7 \text{ kJ}$$

$$C_{(s)} + O_{2(g)} \rightarrow CO_{(g)} + \tfrac{1}{2}O_{2(g)} \qquad \Delta H = -110.4 \text{ kJ}$$

## Standard enthalpy of formation

The **standard enthalpy of formation**, $\Delta H_{f,\,T}^{0}$, of a substance is the standard enthalpy for its formation from its elements in their standard state at a given temperature and pressure.

The standard enthalpy of formation of an element is equal to zero by definition.



# Standard state depends on state of aggregation

| State of Aggregation | Standard State |
| --- | --- |
| Gas | Pressure of 1 atm, 298 K |
| Pure liquid or solid | Pure substance, 298 K |
| Solution | Solute: 1 M, 298 K<br>Solvent: Pure liquid, 298K |

1. $\Delta H_f^0 = 0$ for elements in standard state.
2. Need to select one allotrope of element as reference form.

   $C_{graphite}$ vs. $C_{diamond}$ vs. $C_{60}$

   $S_{rhombic}$ vs. $S_{monoclinic}$
3. $\Delta H_f^0$ varies *slightly* with temperature…we use 298 K as default.

## Standard Enthalpy of Reaction $\Delta_r H^0$:

$$\Delta_r H^0 = \sum_i \nu_i \Delta H^0_{f,i}(\text{products}) - \sum_j \nu_j \Delta H^0_{f,j}(\text{reactants})$$

$\Delta H_f^0$ = Enthalpy of formation for each product / reactant

$\nu$ = Stoichiometric coefficient from reaction equation

# Examples

Calculate the standard enthalpy of reaction for the reaction:

$$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O\,(l)$$

| Substance | $\Delta H_f^0$ / $kJmol^{-1}$ (from the database) |
|---|---|
| $CH_3OH(l)$ | -238.86 |
| $O_2(g)$ | |
| $CO_2(g)$ | -393.51 |
| $H_2O(l)$ | -285.83 |

# Examples

Calculate the standard enthalpy of reaction for the reaction:

$$2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O\,(l)$$

| Substance | $\Delta H_f^0$ / kJmol$^{-1}$ (from the database) | $\nu_i$ |
|---|---|---|
| $CH_3OH(l)$ | -238.86 | 2 |
| $O_2(g)$ | 0 | 3 |
| $CO_2(g)$ | -393.51 | 2 |
| $H_2O(l)$ | -285.83 | 4 |

$$\Delta_r H^0 = \sum_i \nu_i \Delta H^0_{f,i}(\text{products}) - \sum_j \nu_j \Delta H^0_{f,j}(\text{reactants})$$

$$= 4(-285.83) + 2(-393.51) - 3(0.00) - 2(-238.86)$$

$$= -1452.62\ \text{kJ}$$

b) Calculate the standard enthalpy of vaporization for water:

$$H_2O\,(l) \rightarrow H_2O(g)$$

| Substance | $\Delta H_f^0$ / kJmol$^{-1}$ (from the database at 298K) | $\nu_i$ |
|---|---|---|
| $H_2O(l)$ | -285.83 | 1 |
| $H_2O(g)$ | -241.82 | 1 |

$$\Delta H^0 = \sum_i \nu_i \Delta H^0_{f,i}(\text{products}) - \sum_j \nu_j \Delta\ H^0_{f,j}(\text{reactants})$$

$$= -241.82 - (-285.83) = \ 44.01\ \text{kJ}$$

and at 100°C: $\Delta_{vap} H_m = 44.66$ kJ/mol