

# Physical Chemistry I for Biochemists

Chem340

Lecture 14 (2/14/11)

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•Ch4.1-4.4

## Announcement

- Exam 1 will be returned on Friday.
- HW5 is uploaded at the web site. This should be easier.
- Exam 2 will be held 3/18 Right before Spring Break (~4 weeks from now)

## Ch 4.1 Energy Stored in Chemical Bonds is Related or Taken Up in Chemical Reactions

- Significant amount of internal energy or enthalpy is stored in the form of chemical bond.

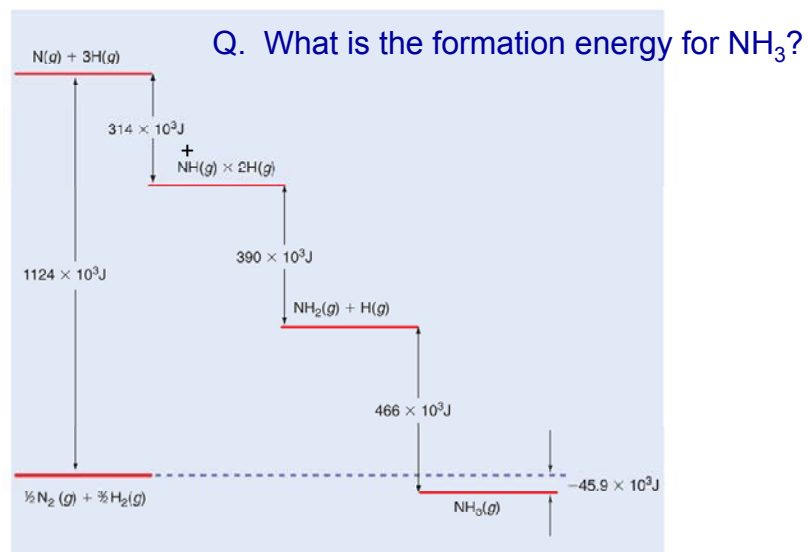
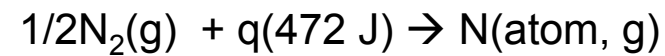


Figure: 04-01

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## Which of $\Delta H$ and $\Delta U$ Should We Use to Characterize Chemical Reactions?

- Since most of reactions are carried out at a constant pressure, we use  $\Delta H$  rather than  $\Delta U$  to measure the change in the energy associated with chemical reaction.

Constant Volume  $\rightarrow \Delta U$

Constant Pressure  $\rightarrow \Delta H$

$$\begin{aligned}\text{For an ideal gas, } \Delta H &= \Delta(U+PV) = \Delta U + \Delta(nRT) \\ &= \Delta U + RT\Delta n\end{aligned}$$

(see Example 4.2 p69; Sec 4.5) (if  $T = \text{const}$ )

## Standard Partial Molar Enthalpy

(Raff p105)

For a molecule A,

- $dH_A = C_{pA}dT + (\partial H/\partial P)dP + \bar{H}_A dn_A$

$$\bar{H}_A = \left( \frac{\partial H}{\partial n_A} \right)_{T,P} \text{ is the partial molar enthalpy of A.}$$

- At the standard condition ( $T = 298.15 \text{ K}$ ,  $P = 1 \text{ bar}$ )

$$dH_A = \bar{H}_A dn_A \rightarrow \Delta H_A = \bar{H}_A \Delta n_A$$

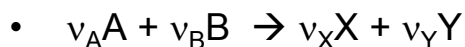
If we have more than one type of molecule,

$$\Delta H = \Delta n_A \bar{H}_A + \Delta n_B \bar{H}_B + \Delta n_C \bar{H}_C + \dots = \sum_X \Delta n_X \bar{H}_X$$

## Reaction Enthalpy using Partial Molar Enthalpy

- For a reaction that takes place at constant P and T, the heat flow needed for a chemical reaction is

$$\Delta H_{\text{reaction}}$$



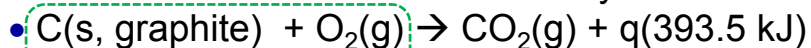
$$\Delta H_{\text{reaction}} = v_X \bar{H}_X + v_Y \bar{H}_Y - v_A \bar{H}_A - v_B \bar{H}_B$$

$$\Delta H_{\text{reaction}} = \sum_{i=X} v_i^{\text{Product}} \bar{H}_i - \sum_{k=A} v_k^{\text{Reactant}} \bar{H}_k$$

- In general, it is difficult to find partial molar enthalpy.  $\rightarrow$  We use formation enthalpy.

## Standard Formation Enthalpy

- Consider a reaction from **pure elements** that are most stable **at 298.15 K and 1 bar**, which results in the formation of one mole of a molecule of your interest.



Note, the only product should be the molecule of your interest.

- Assume that q is the heat generated for the reaction when P = 1 bar and T = 298.15K (Standard State). The energy is described as a standard formation enthalpy  $\Delta H_f^0$  for  $\text{CO}_2(\text{g})$  and  $\text{NH}_3(\text{g})$  as

$$\Delta H_f^0 \text{ for } \text{CO}_2 = -393.5 \text{ kJmol}^{-1}$$

$$\Delta H_f^0 \text{ for } \text{NH}_3 = -45.9 \text{ kJmol}^{-1}$$

## Standard Formation Enthalpy Listed in Appendix B Table 4.1

Substance	$\Delta H_f^0(\text{kJ mol}^{-1})$
<b>Carbon</b>	You can tell which compound is more stable!
Graphite(s)	0
Diamond(s)	1.89
C(g)	716.7
CO(g)	-110.5
<b>Nitrogen</b>	
N <sub>2</sub> (g)	0
N(g)	472.7
NH <sub>3</sub> (g)	-45.9
NO(g)	91.3
NO <sub>2</sub> (g)	81.6

## Reaction Enthalpy using Standard Formation Enthalpy

- For a reaction that takes place at constant P and T, the heat flow needed for a chemical reaction is

$$\Delta H_{\text{reaction}}$$



$$\Delta H_{\text{reaction}} = [\text{Q1}]$$

- In general,

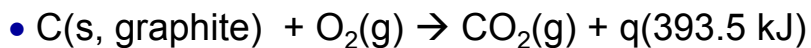
$$\Delta H_{\text{reaction}} = \sum_{i=X} v_i^{\text{Product}} \Delta H_{f,i}^0 - \sum_{k=A} v_k^{\text{Reactant}} \Delta H_{f,k}^0$$

or

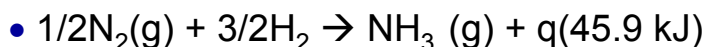
$$\Delta H_{\text{reaction}} = \sum_i v_i \Delta H_{f,i}^0$$

(Note use  $v_i > 0$  for products and  $v_i < 0$  for reactants)

## Reaction Enthalpy from Standard Formation Enthalpy (Example)



$$\begin{aligned}\Delta H_{\text{reaction}} &= \Delta H_f^0(\text{CO}_2(\text{g})) - \Delta H_f^0(\text{O}_2(\text{g})) - \Delta H_f^0(\text{C(s, graphite)}) \\ &= \Delta H_f^0(\text{CO}_2(\text{g})) = -393.5 \text{ kJ}\end{aligned}$$



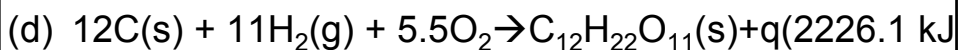
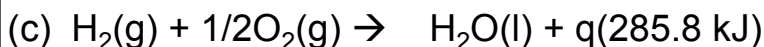
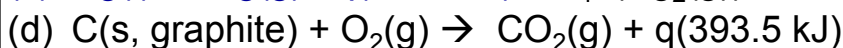
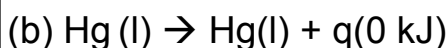
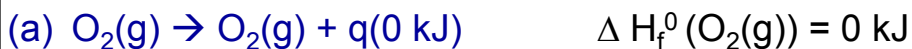
$$\begin{aligned}\Delta H_{\text{reaction}} &= \Delta H_f^0(\text{NH}_3(\text{g})) - (1/2)\Delta H_f^0(\text{N}_2(\text{g})) - (3/2)\Delta H_f^0(\text{H}_2(\text{g})) \\ &= \Delta H_f^0(\text{NH}_3(\text{g})) = -45.9 \text{ kJ}\end{aligned}$$

$$\Delta H_f^0 \text{ for CO}_2 = -393.5 \text{ kJmol}^{-1}$$

$$\Delta H_f^0 \text{ for NH}_3 = -45.9 \text{ kJmol}^{-1}$$

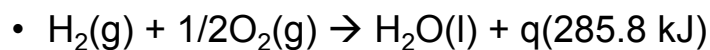
## Sample Question

- Write reactions to obtain standard formation enthalpy of (a)  $\text{O}_2(\text{g})$ , (b)  $\text{Hg}(\text{l})$ , (c)  $\text{Hg}(\text{g})$ , (d)  $\text{CO}_2(\text{g})$ , (e)  $\text{H}_2\text{O}(\text{l})$  (f)  $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$

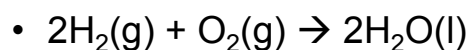


## Quiz

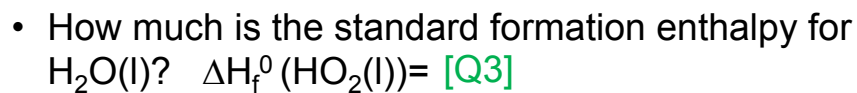
How much is the reaction enthalpy for the following reactions at  $T = 293.15\text{K}$  and  $P = 1\text{ bar}$ ?



$$\Delta H_{\text{reaction}}^0 = \text{[Q1]}$$



$$\Delta H_{\text{reaction}}^0 = \text{[Q2]}$$



## Sample Question

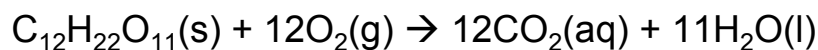
### Ex. 4.1 (p67)

$$\Delta H_f^0(\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})) = -2226\text{ kJmol}^{-1}$$

$$\Delta H_f^0(\text{CO}_2(\text{aq})) = -412.9\text{ kJmol}^{-1}$$

$$\Delta H_f^0(\text{H}_2\text{O}(\text{l})) = -258.8\text{ kJmol}^{-1}$$

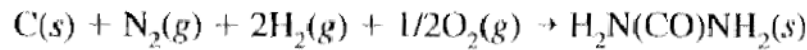
- How much is the reaction enthalpy for the following reaction?



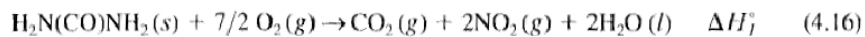
$$\begin{aligned}\Delta H_{\text{reaction}} &= v_X H_{fX}^0 + v_Y H_{fY}^0 - v_A H_{fA}^0 - v_B H_{fB}^0 \\ &= 12H_f^0(\text{CO}_2(\text{aq})) + 11H_f^0(\text{H}_2\text{O}(\text{l})) - H_f^0(\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})) \\ &\quad - H_f^0(\text{O}_2(\text{g})) \\ &= 12(-412.9\text{kJ}) + 11(-258.8\text{kJ}) - (-2226\text{ kJ}) = -5873\text{kJ}\end{aligned}$$

## Hess's Law is Based on Enthalpy Being a State Function

- How can we  $\Delta H_f^0$  calculate from known reaction enthalpy  $\Delta H_{\text{reaction}}$ ? For example

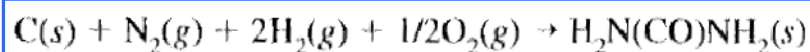
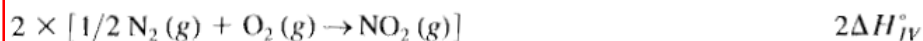
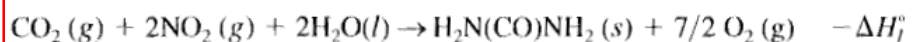
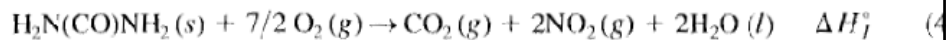
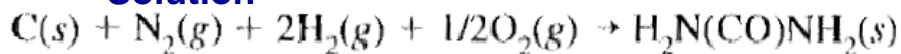


is the reaction to obtain  $\Delta H_f^0(\text{urea}(s))$ , but this reaction does not happen readily. Instead, we use



**Q.** How to obtain  $\Delta H_f^0(\text{urea}(s))$ ?

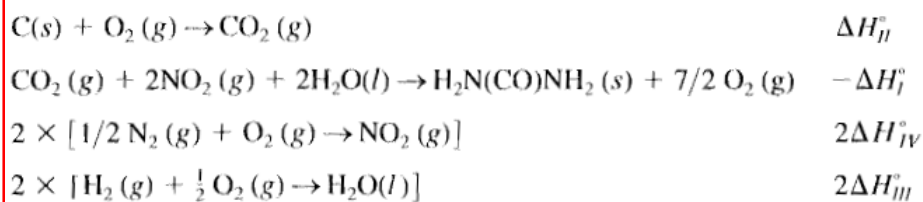
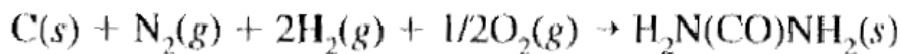
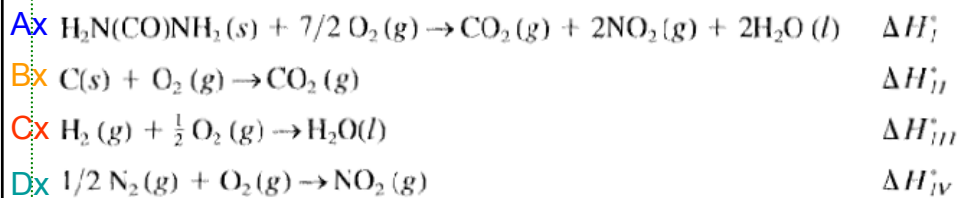
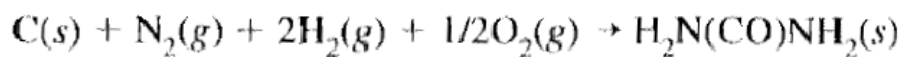
### Solution



$$\Delta H_f^\circ = -\Delta H_I^\circ + \Delta H_{II}^\circ + 2\Delta H_{III}^\circ + 2\Delta H_{IV}^\circ$$



### Alternative Solution



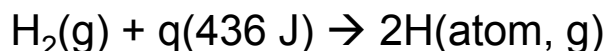
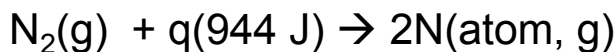
### Bond Enthalpy

#### Sample Question (Example 4.2)

- The **average bond enthalpy** of the O-H bond in water is defined as one-half of the enthalpy change for the reaction  $\text{H}_2\text{O}$ .



What is the bond enthalpy obtained from the following reactions for  $\text{N}_2$  and  $\text{H}_2$ ?



Q. How about the bond for  $\text{NH}_3(g)$ ?

Q. What is the average bond energy for NH<sub>3</sub>?

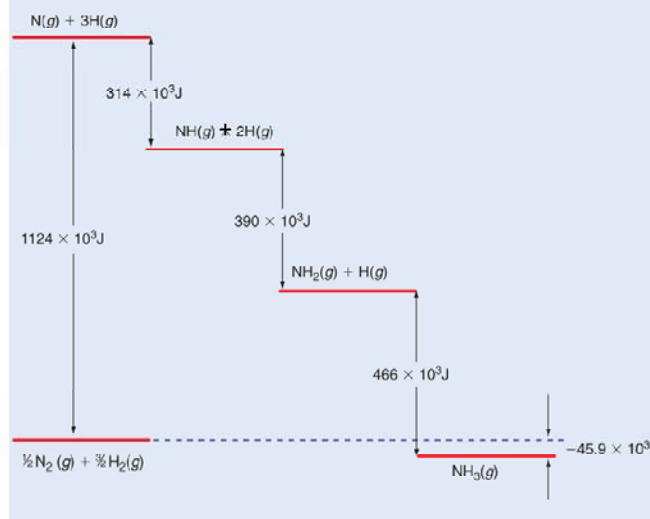


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## 4.4 The Temperature Dependence of Reaction Enthalpies

Suppose we would like to perform a reaction at a higher temperature than 298.15K, the enthalpy can be calculated from

$$\bullet H_T^0 = H_{298.15\text{K}}^0 + \int_{298.15\text{K}}^T C_p(T') dT'$$

For a reaction

$$\Delta H_{reaction,T}^0 = \Delta H_{reaction,298.15\text{K}}^0 + \int_{298.15\text{K}}^T \Delta C_p(T') dT'$$

$$\Delta C_p(T') = \sum \nu_j C_{p,j}(T')$$

#### EXAMPLE PROBLEM 4.1

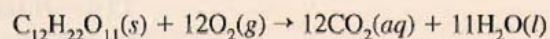
Using the data:

$$\Delta H_f^\circ (\text{C}_{12}\text{H}_{22}\text{O}_{11},s) = -2226.1 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ (\text{CO}_2,aq) = -412.9 \text{ kJ mol}^{-1} \text{ and}$$

$$\Delta H_f^\circ (\text{H}_2\text{O},l) = -285.8 \text{ kJ mol}^{-1}$$

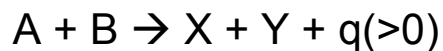
calculate the heat evolved in the oxidation of 1 mol of sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11},s$ ) to  $\text{CO}_2(aq)$  and water ( $l$ ) at 1 bar:



Molar mass of sucrose ~342 g

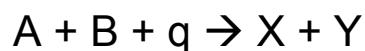
## Two Type of Reactions and Reaction Enthalpy

**Exothermic Reaction:** Heat is generated after a reaction. (T is increased).



$$\Delta H < 0$$

**Endothermic Reaction:** Heat is needed for a reaction. (T is decreased).



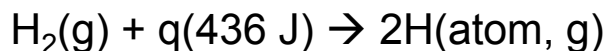
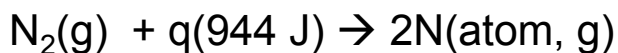
$$\Delta H > 0$$

## Bond Enthalpy Sample Question (Example 4.2)

- The **average bond enthalpy** of the O-H bond in water is defined as one-half of the enthalpy change for the reaction  $\text{H}_2\text{O}$ .



What is the bond enthalpy obtained from the following reactions for  $\text{N}_2$  and  $\text{H}_2$ ?



Q. How about the bond for  $\text{NH}_3(g)$ ?

Q. What is the average bond energy for  $\text{NH}_3$ ?

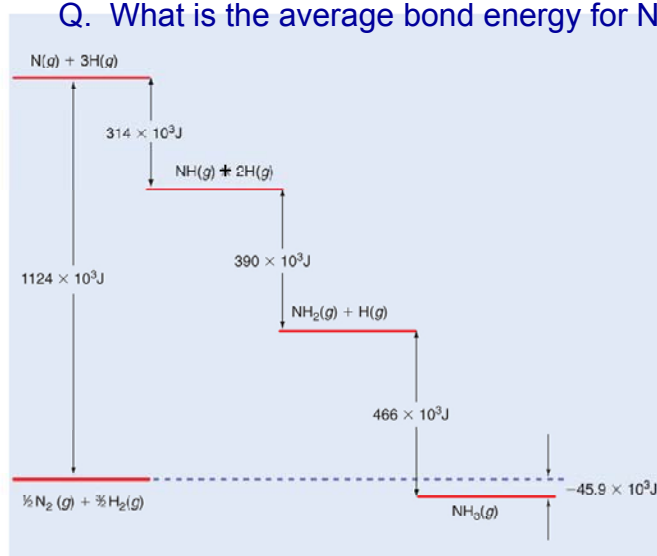


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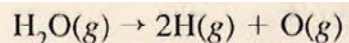
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## Bond Energy: $\Delta U$ for Reactions for a Bond Formation (P69)

### EXAMPLE PROBLEM 4.2

The average **bond enthalpy** of the O—H bond in water is defined as one-half of the enthalpy change for the reaction  $\text{H}_2\text{O}(g) \rightarrow 2\text{H}(g) + \text{O}(g)$ . The formation enthalpies,  $\Delta H_f^\circ$ , for  $\text{H}(g)$  and  $\text{O}(g)$  are 218.0 and 249.2  $\text{kJ mol}^{-1}$ , respectively, at 298.15 K, and  $\Delta H_f^\circ$  for  $\text{H}_2\text{O}(g)$  is  $-241.8 \text{ kJ mol}^{-1}$  at the same temperature.

- a. Use this information to determine the average bond enthalpy of the O—H bond in water at 298.15 K.



$$\Delta H_{\text{bond}}^0 = \Delta H_{\text{reaction}}^0 / 2$$

$$\begin{aligned} \Delta H_{\text{reaction}}^0 &= 2\Delta H_f^0(\text{H}(g)) + \Delta H_f^0(\text{O}(g)) - \Delta H_f^0(\text{H}_2\text{O}(g)) \\ &= 218.0 \times 2 \text{ kJ} + 249.2 \text{ kJ} - (-241.8 \text{ kJ}) = 927 \text{ kJ} \end{aligned}$$

- b. Determine the average **bond energy**,  $\Delta U$ , of the O—H bond in water at 298.15 K. Assume ideal gas behavior.

$$\Delta U_{\text{reaction}}^0 = \Delta H_{\text{reaction}}^0 - \Delta(PV) = \Delta H_{\text{reaction}}^0 - RT\Delta(n)$$

Q. What is  $\Delta n$ ?

## 4.4 The Temperature Dependence of Reaction Enthalpies

Suppose we would like to perform a reaction at a higher temperature than 298.15K, the enthalpy can be calculated from

$$\bullet H_T^0 = H_{298.15 \text{ K}}^0 + \int_{298.15 \text{ K}}^T C_p(T') dT'$$

For a reaction

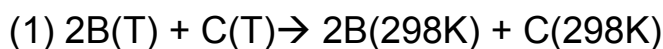
$$\Delta H_{\text{reaction}, T}^0 = \Delta H_{\text{reaction}, 298.15 \text{ K}}^0 + \int_{298.15 \text{ K}}^T \Delta C_p(T') dT'$$

$$\Delta C_p(T') = \sum \nu_j C_{p,j}(T')$$

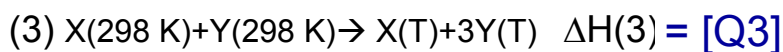
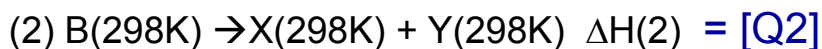
## HW5 Q1

- Using  $dH_A = C_{pA}dT + (\partial H/\partial P)_{T,n}dP + (\partial H/\partial n)_{T,P}dn_A$  (A = B, X, or Y), prove that the reaction enthalpy  $\Delta H_{\text{reaction}}(T)$  is given by eq. (4.27) in the text. Specify the path of (P, T, n) you would like to use. Assume a reaction  $2B + C \rightarrow X + 3Y$ .

$$\Delta H^0_{\text{reaction},T} = \Delta H^0_{\text{reaction},298.15K} + \int_{298.15K}^T \Delta C_p(T')dT'$$



$\Delta H(1) = [Q1]$



## 4.5 The Experimental Determination of $\Delta U$ and $\Delta H$ for Chemical Reactions

No heat flow  $\rightarrow q = 0$

$$\Delta U_{\text{overall}} = 0$$

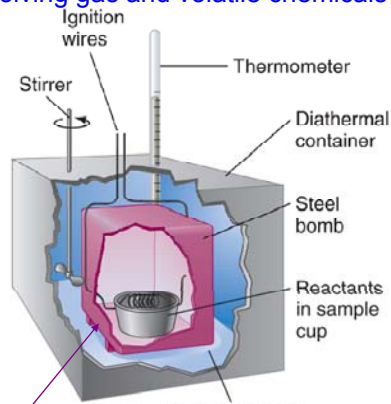
$$\Delta U_{\text{overall}} = \frac{m_S}{M_S} \Delta U_{\text{reaction}}$$

$$+ \frac{m_{H_2O}}{M_{H_2O}} C_{H_2O,m} \Delta T$$

$$+ C_{\text{calorimeter}} \Delta T$$

Measured

Bomb Calorimeter for Reaction involving gas and volatile chemicals



$V = \text{Const}$  for the container

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For ideal gas,

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + RT(\Delta n)$$