

# Thermodynamics tutorhour 2

November 15<sup>th</sup> 2023

- Questions about the lecture or course matter?
- Reaction Enthalpy and Kirchhoffs Law
- The Bomb Calorimeter

## How much heat is released during a chemical reaction?

If the reaction takes place under normal (laboratory) conditions, we may assume that the pressure is not influenced by the reaction.

$$q_p = \Delta H$$

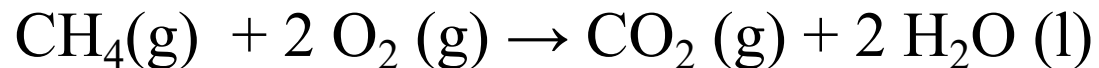
$\Delta_r H^\ominus$  is defined as the  $\Delta_f H^\ominus$  (products) –  $\Delta_f H^\ominus$  (reactants)

The  $\Delta_f H^\ominus$  of elements = 0.

In formula:

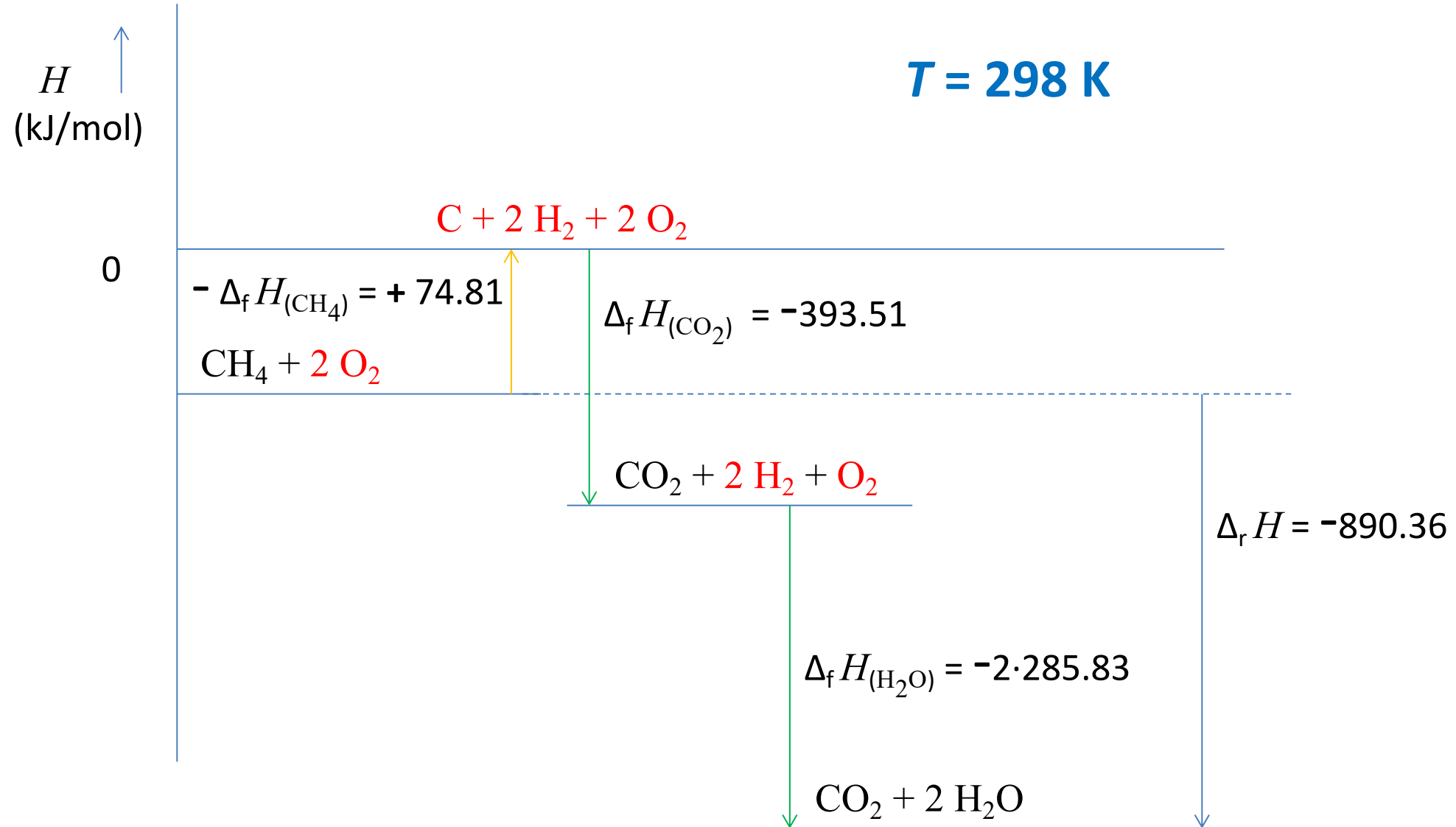
$$\Delta_r H = \sum H_{f,products} - \sum H_{f,reactants}$$

For example: the combustion of methane



$$\Delta_r H = -(-74.81) - 2 \cdot 0 + (-393.51) + 2 \cdot (-285.83) = -890.36 \text{ kJ/mol CH}_4$$

# The combustion of methane in an enthalpy diagram:



In the data section of Atkins one can find  $\Delta_f H^\ominus$  at **298 K**.

Often reactions occur at another temperature, in which case a correction is needed.

### For example:

Substance S is being heated (at constant pressure) from  $T_A$  (below melting point,  $T_{fus}$ ) to  $T_X$  (above boiling point,  $T_{vap}$ ). The heat needed for this process can be calculated using this formula:

$$\Delta H = \int_{T_A}^{T_{fus}} C_{p,solid} dT + \Delta_{fus} H + \int_{T_{fus}}^{T_{vap}} C_{p,liquid} dT + \Delta_{vap} H + \int_{T_{vap}}^{T_X} C_{p,gas} dT$$

### A common approximation:

$c_p$  is constant over a certain temperature interval. In such cases,  $c_p$  can be placed in front of the integral sign:

$$\Delta H = \int_{T_1}^{T_2} C_p dT = C_p \int_{T_1}^{T_2} dT = C_p \Delta T$$

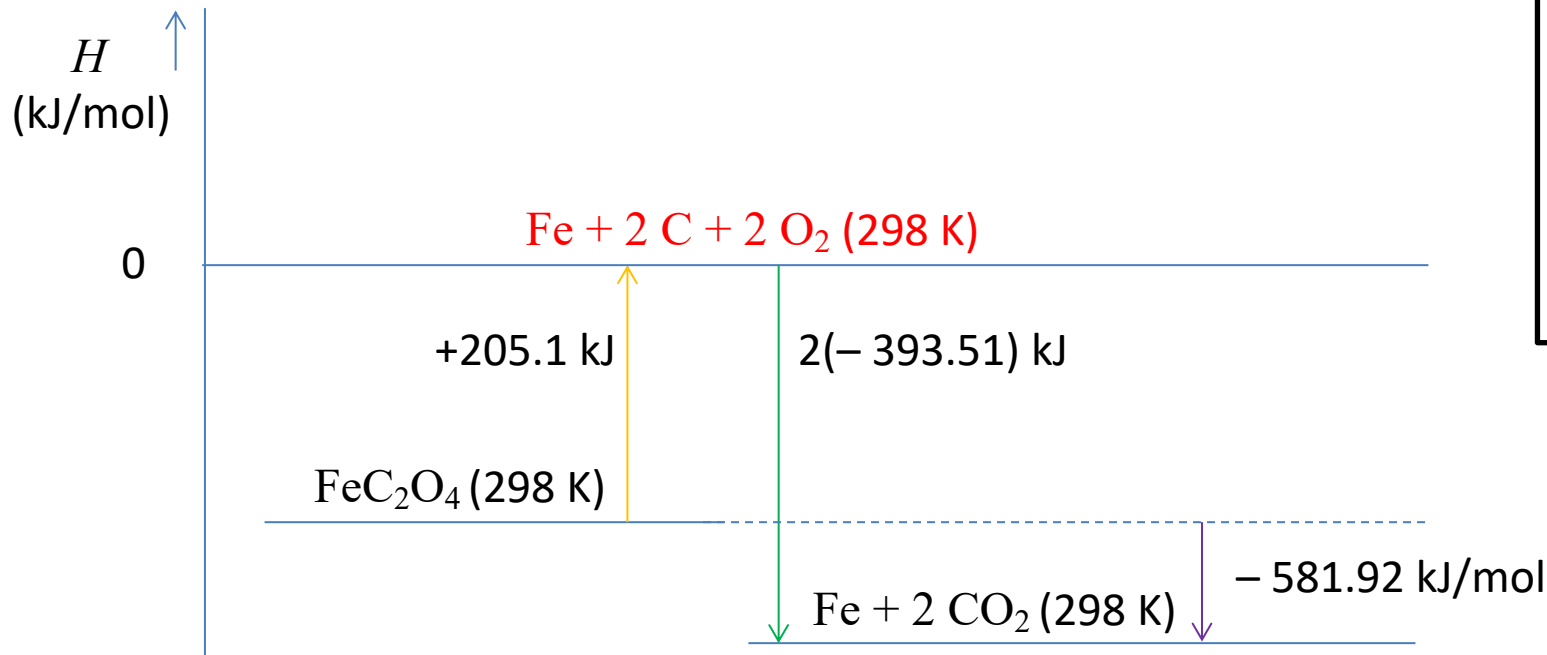
## An Example Iron(II) oxalate

Iron(II) oxalate ( $\text{FeC}_2\text{O}_4$ ) is a yellow solid. When iron(II) oxalate is heated, it decomposes into iron and carbon dioxide:  $\text{FeC}_2\text{O}_4 \rightarrow \text{Fe} + 2 \text{CO}_2$

**Question 1** Calculate  $\Delta_r H_{(298 \text{ K})}$  for this reaction. You may want to use an enthalpy diagram.

$$\begin{aligned}\Delta_r H_{(298 \text{ K})} &= -(\Delta_f H_{(298 \text{ K}, \text{FeC}_2\text{O}_4)}) + \Delta_f H_{(298 \text{ K}, \text{Fe})} + 2 \cdot (\Delta_f H_{(298 \text{ K}, \text{CO}_2)}) \\ &= -(-205.1 \text{ kJ mol}^{-1}) + 0 + 2 \cdot (-393.51 \text{ kJ mol}^{-1}) = -581.92 \text{ kJ/mol}\end{aligned}$$

In an enthalpy diagram:



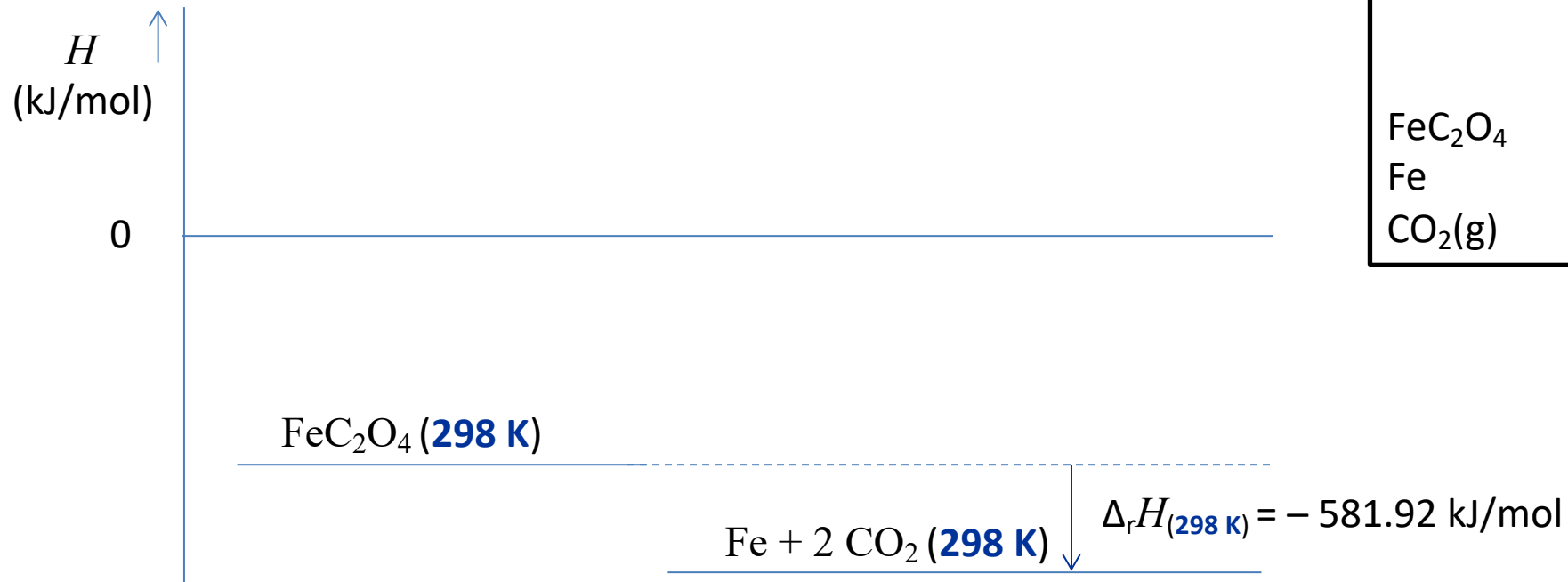
### Thermodynamic data (all values at $T=298 \text{ K}$ )

	$\Delta_f H^\ominus / (\text{kJ mol}^{-1})$	$C_{p,m}^\ominus / (\text{J K}^{-1} \text{ mol}^{-1})$
$\text{FeC}_2\text{O}_4$	-205.1	105
Fe		25.69
$\text{CO}_2(\text{g})$	-393.51	37.11

## An Example Iron(II) oxalate

There is a problem... we calculated the enthalpy of the reaction at 25°C. However, the reaction will not take place at 25°C. The decomposition will take place at a significant rate at a temperature of at least 423 K. The  $\Delta_f H^\ominus$  at 423 K is not listed in the resource section.

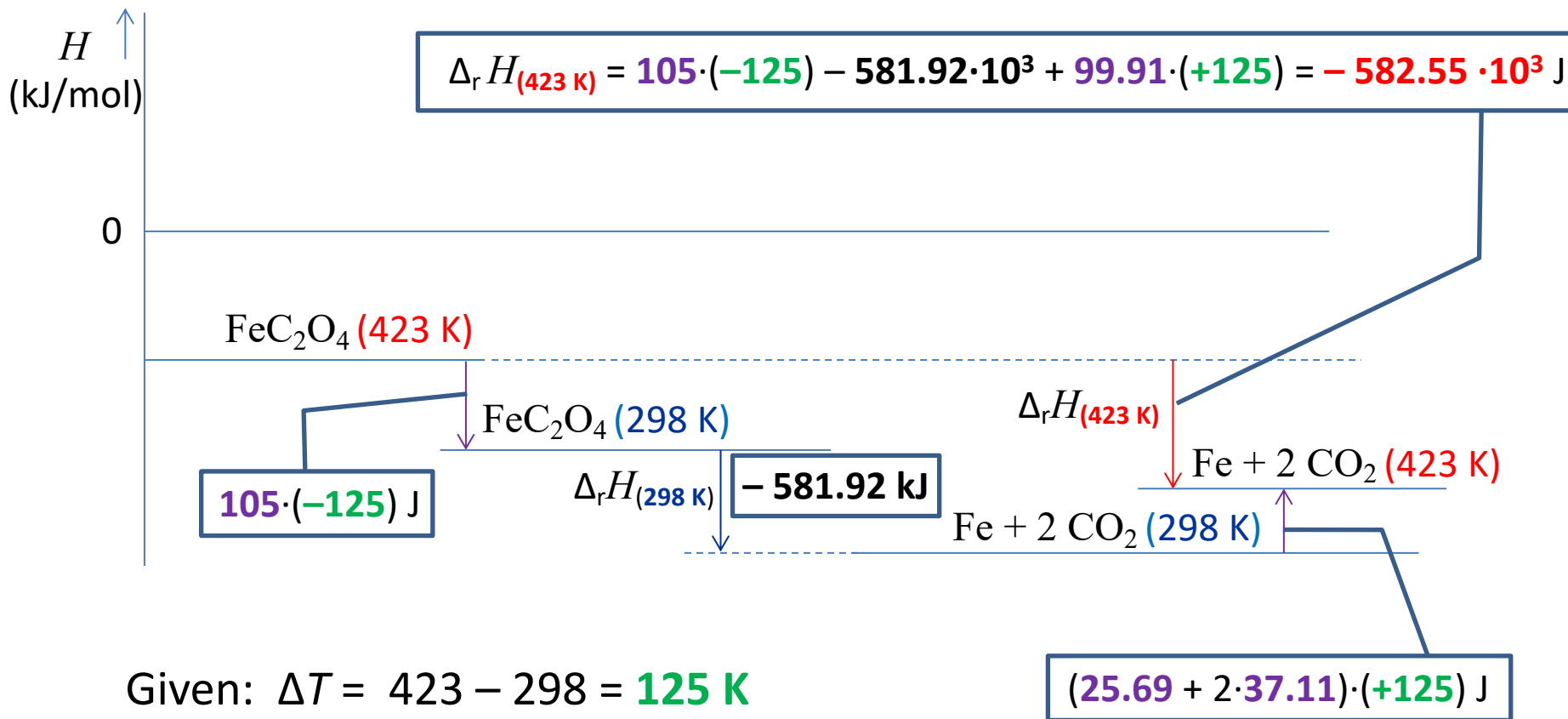
**Question 2** Draw an alternative path with which one can calculate  $\Delta_f H^\ominus$  at 423 K and explain how it can be used to calculate  $\Delta_r H^\ominus$  (423 K)



### Thermodynamic data (all values at T=298 K)

	$\Delta_f H^\ominus / (\text{kJ mol}^{-1})$	$C_{p,m}^\ominus / (\text{J K}^{-1} \text{mol}^{-1})$
$\text{FeC}_2\text{O}_4$	-205.1	105
Fe		25.69
$\text{CO}_2(\text{g})$	-393.51	37.11

The alternative path in the enthalpy diagram:



Given:  $\Delta T = 423 - 298 = 125 \text{ K}$

and  $\Delta H = C_p \Delta T$

So:  $\Delta_r H_{(423\text{ K})} = -582.55 \text{ kJ mol}^{-1}$

This approach is Kirchoff's law:

$$\Delta_r H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2} \Delta c_p dT$$

### Question 3

Now, calculate  $\Delta_r H_{(423\text{ K})}$  using the relation

$$\Delta H = \int_{T_1}^{T_2} C_p dT = C_p \Delta T$$

Thermodynamic data (all values at T=298 K)

	$\Delta_f H^\ominus / (\text{kJ mol}^{-1})$	$C_{p,m}^\ominus / (\text{J K}^{-1} \text{ mol}^{-1})$
FeC <sub>2</sub> O <sub>4</sub>	-205.1	105
Fe		25.69
CO <sub>2</sub> (g)	-393.51	37.11

# The change in reaction enthalpy

Reaction Enthalpy at 298 K = - 581.92 kJ

Reaction Enthalpy at 432 K = - 582.55 kJ

**Difference:**  $\Delta_r H_{(298\text{ K})} - \Delta_r H_{(423\text{ K})} = - 581.92 - (- 582.55) = 0.63\text{ kJ}$

As a percentage of  $\Delta_r H_{(298\text{ K})}$ :  $(0.63 / 581.92) \times 100\% = 0.11\%$

## Conclusion:

The reaction enthalpy is relatively independent of temperature, especially when there are no phase changes.



# Bomb calorimeter

Isolated water bath with reactor vessel; measures temperature change at constant volume (isochoric).

## Two steps:

- 1 Determine  $C_V$  of the calorimeter
- 2 Use that  $C_V$  to measure unknown reaction enthalpy

### Ad 1:

- Ignite a sample with known  $\Delta_r U$  (internal reaction energy) and measure  $\Delta T$

- Since the volume is constant:  $\Delta_r U = q + w = q + 0 = C_V \Delta T$

$$\text{Thus: } C_V = \Delta_r U / \Delta T$$

### Ad 2:

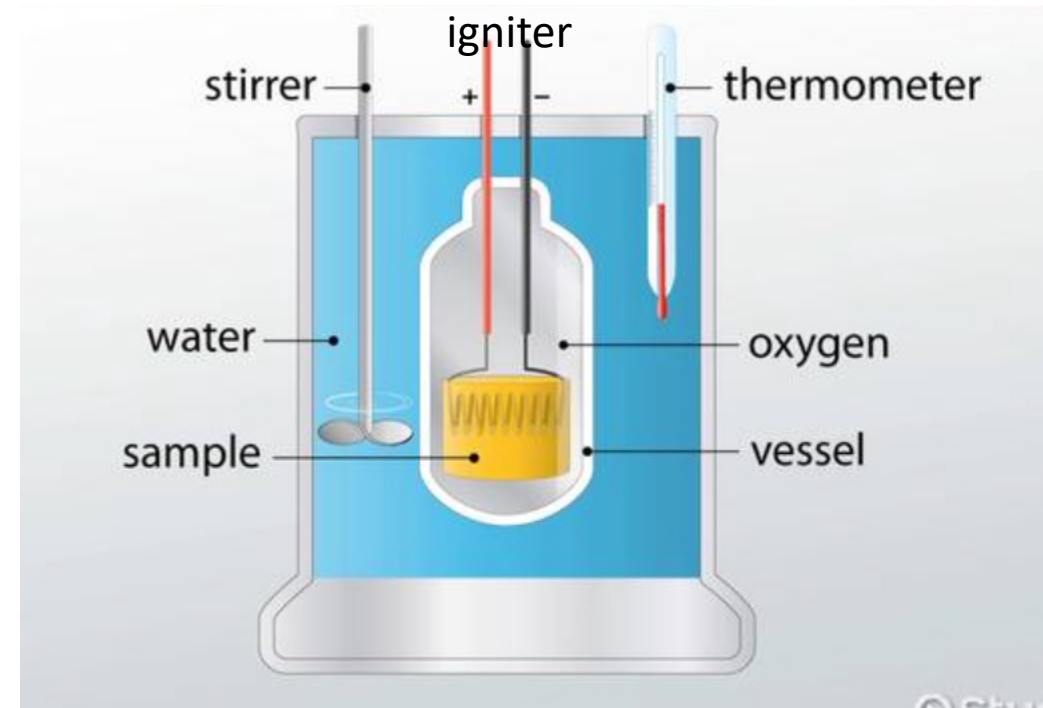
- Ignite the sample of interest and measure  $\Delta T$

- Since  $dH = dU + d(pV)$  and  $dU = C_V dT$  and  $pV = nRT$

$$dH = dU + d(nRT) = C_V dT + (RT)dn + (nR)dT$$

- When temperature change is small:  $dH = C_V dT + (RT)dn$  ( $C_V dT$  is not negligible, because  $C_V$  of the bomb calorimeter is very large, much larger than  $nR$ !)

$$\Delta_r H = \int dH = C_V \int_{T_1}^{T_2} dT + RT \int_{n_1}^{n_2} dn = C_V \Delta T + RT \Delta n$$



**THE END**