

Topics

- First Law of Thermodynamics Applied to Combustion
- Constant Volume Combustion
- Constant Pressure Combustion
- Enthalpy of Formation
- Heating Values of Fuels

1. The First Law of Thermodynamics

This is a statement that energy is conserved. It applies to an identifiable system of material. For now, let this system be a mixture of gases such as air and vaporized fuel.

Let a system undergo changes from a state 1 to state 2.

- Q is heat transferred into the system as it undergoes the change.
- W is work done by the system on surroundings, in our case pV work.
- U stands for internal energy. ΔU is change in this quantity as the system state changes from 1 to 2.

We have that

$$Q - W = \Delta U$$

saying that the net energy exchanged with the surroundings through heat and work balances the net change in internal energy.

Furthermore, at 1 the internal energy belongs to material to be combusted called reactants. At 2 the internal energy is that of material that is combusted called products.

$$Q - W = U_P - U_R$$

The products P and reactants R can be at the same or different temperatures and pressures.

2. Constant Volume Process

Since the only type of work we allow is pV work

$$W = \int_{V_1}^{V_2} p dV$$

and there being no volume change, there is no work. Consequently,

$$Q = \Delta U = U_P - U_R$$

Now arrange things so the final temperature of the products is the same as the initial temperature of the reactants.

$$Q = (\Delta U)_{V,T}$$

Note that both Q and $(\Delta U)_{V,T}$ are negative. In this case, Q is called the heat of reaction at constant volume and temperature T .

- This kind of special constant volume combustion is produced in a bomb calorimeter, a closed vessel in which fuel is vaporized and burned, and the vessel is cooled back to its starting temperature while the amount of heat transferred out may be measured.
- There is also constant volume combustion, *approximately* in SI engines where combustion takes place rapidly near TDC. This is not exactly what happens, it's just a model.

3. Constant Pressure Combustion

The work may be calculated easily. Since we are integrating a constant.

$$W = \int_{V_R}^{V_P} p dV = pV_P - pV_R$$

Substitute this into the First Law.

$$Q - W = Q - (pV_P - pV_R) = \Delta U = U_P - U_R$$

$$Q = (U_P + pV_P) - (U_R + pV_R)$$

The grouping $U + pV$ is called enthalpy, H .

$$Q = H_P - H_R = \Delta H$$

describes constant pressure combustion. In the special case where products are allowed to cool to the initial temperature of reactants, i.e constant temp.

$$Q = (\Delta H)_{p,T}$$

Here Q is called the heat of reaction at constant pressure and temperature, T .

- This kind of special constant pressure combustion is produced in a continuous flow calorimeter, an open vessel in which fuel is vaporized and burned, and the vessel is cooled back to its starting temperature while the amount of heat transferred out may be measured.
- There is also constant pressure combustion, *approximately* in CI engines where combustion takes place at nearly constant pressure, at least partially. This is not exactly what happens, it's just a model.

4. Enthalpy of Formation

When we calculate the enthalpies of reactants and products, we need to ensure that the enthalpy of each species is referred to a common reference.

Definition: enthalpy of formation is the enthalpy change associated with forming one mole of the compound from its elements with each substance in the state of 1 atm pressure at the given temp.

The given temp is often 298.15 K.

$$\Delta \tilde{h}_f^{\circ} = \sum_{\text{products}} n_i \Delta \tilde{h}_{f,i}^{\circ} - \sum_{\text{reactants}} n_i \Delta \tilde{h}_{f,i}^{\circ}$$

Elemental substances, eg O₂, N₂ have enthalpies of formation of 0 at this temperature.

We will demonstrate this for a number of substances. We will use EES.

Please note how easy it is for ideal gas substances.

Here is an excerpt from the "Help" on the Enthalpy function.

ENTHALPY

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The reference state upon which the value of enthalpy is based varies with the substance. However, all ideal gas substances (which have a chemical symbol name, e.g., N₂, CO₂, CH₄) have enthalpy values corresponding to JANAF table references. The JANAF table reference for enthalpy is based on the elements having an enthalpy value of 0 at 298 K (537 R).

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We will see a quick demo. Compare with Table 3.2.

5. Heating Values of Fuels

Many fuels are very complex mixtures of different species. (Typical gasoline may have 100 compounds in it.)

So they can't compute the heat of these fuels in a simple way, so they turn to experiment.

- Burn the fuel in a calorimeter.
- Make sure that combustion is complete. All C in CO₂.

Two heating values

$$Q_{\text{HVP}} = (\Delta H)_{p,T}$$

is called the heating value at constant pressure.

$$Q_{\text{HVV}} = (\Delta U)_{V,T}$$

is called the heating value at constant volume.

But there is a difficulty. Water is a product. Do we measure energy when it is still gaseous, or wait until it is condensed into liquid?

- Not condensed to liquid gives the lower heating value.
- Condense water gives the higher heating value.

The two heating values at constant pressure relate as follows

$$Q_{\text{HHVP}} = Q_{\text{LHVP}} + \left(\frac{m_{\text{H}_2\text{O}}}{m_{\text{fuel}}} \right) h_{\text{fg,H}_2\text{O}}$$

The quantity $h_{\text{fg,H}_2\text{O}}$ is the heat of vaporization of water.

Let me give you a quick demonstration. We will calculate these heating values for propane based on the heat of reaction. See the EES commands posted at the website.