Absolute Enthalpy & Enthalpy of Formation

- Absolute enthalpy = sum of enthalpy = (energy of chemical bonds) + (sensible enthalpy change)

$$\bar{h}_i(T) = \bar{h}^o_{f,i}(T_{ref}) + \Delta \bar{h}_{s,i}(T_{ref})$$

Absolute enthalpy at temp T

Enthalpy of formation at std. Ref. state (T_{ref}, P^o)

Sensible enthalpy change going from T_{ref} to T

$$\Delta \bar{h}_{s,i}(T_{ref}) \equiv \bar{h}^{o}_{f,i}(T_{ref}) - \bar{h}_i(T)$$

Ref. state: T_{ref} = 25°C (298.15 K)

$P_{ref} = P^o$ = 1 atm

Enthalpy of formation, $\bar{h}^{o}_{f} \equiv 0$ for <u>elements</u> in naturally occurring state at ref. state

Oxygen	O_2	gas
Nitrogen	N_2	gas
Carbon	C	solid (graphite)

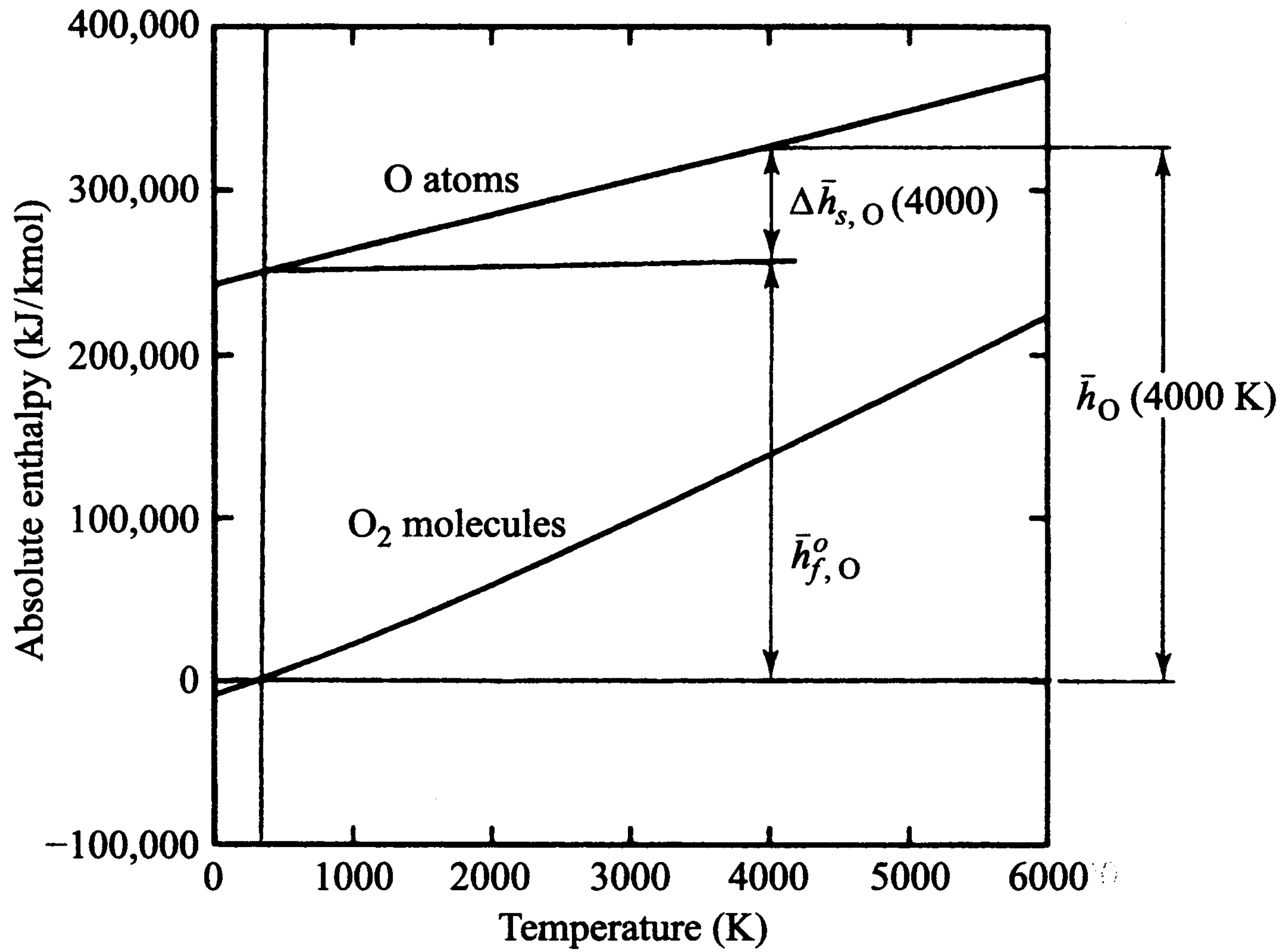

Figure 2.6 Graphical interpretation of absolute enthalpy, heat of formation, and sensible enthalpy.

Enthalpy of Combustion

Enthalpy of Combustion = enthalpy of reaction, Δh_R

Heat of combustion= heating value Δh_c

$$\Delta h_c = -\Delta h_R$$

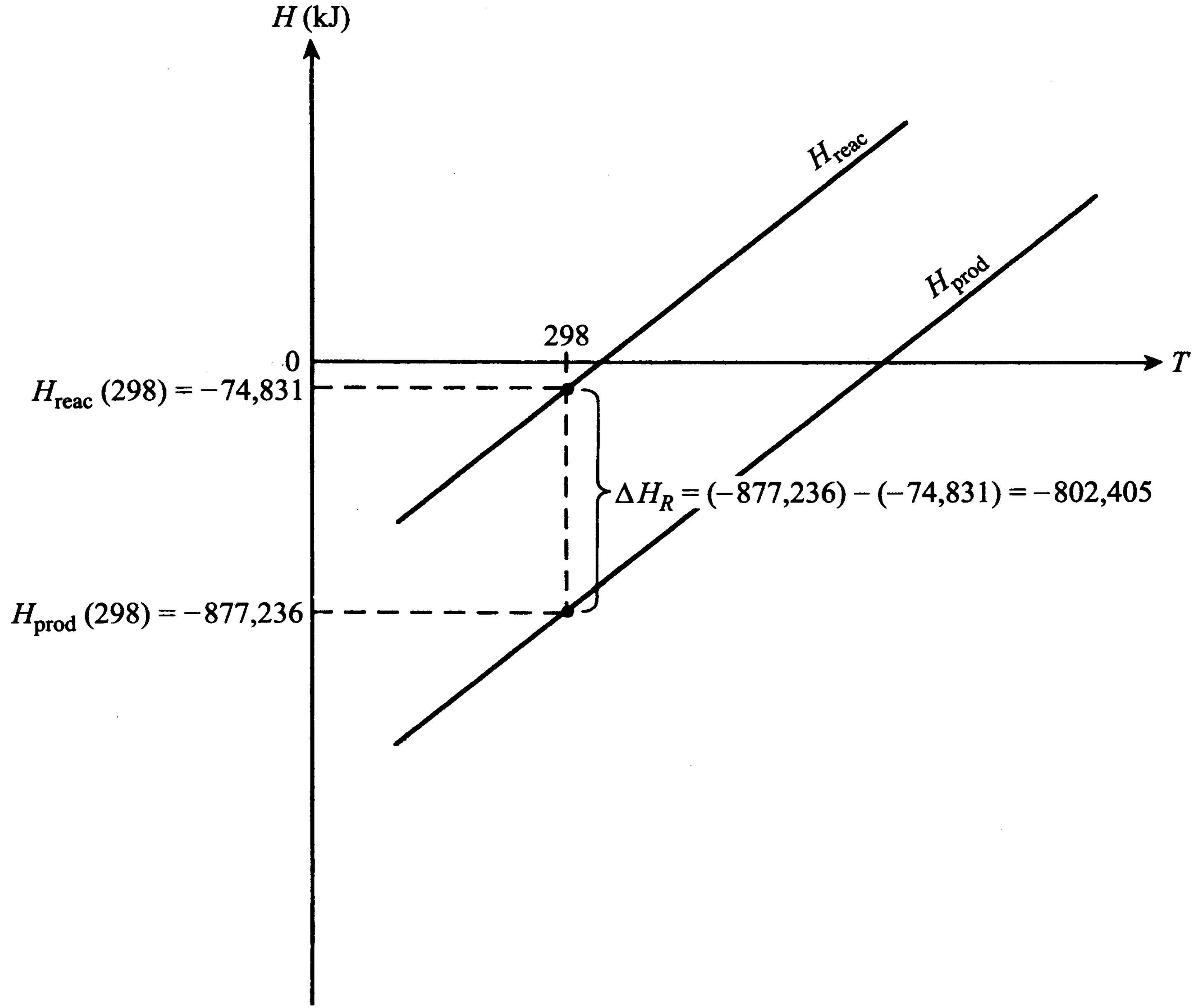

Figure 2.8 Enthalpy of reaction using representative values for a stoichiometric methane–air mixture. The water in the products is assumed to be in the vapor state.

HHV = higher heating value (assuming H_2O in products condensed into liquid)

LHV = lower heating value (assuming no condensation)

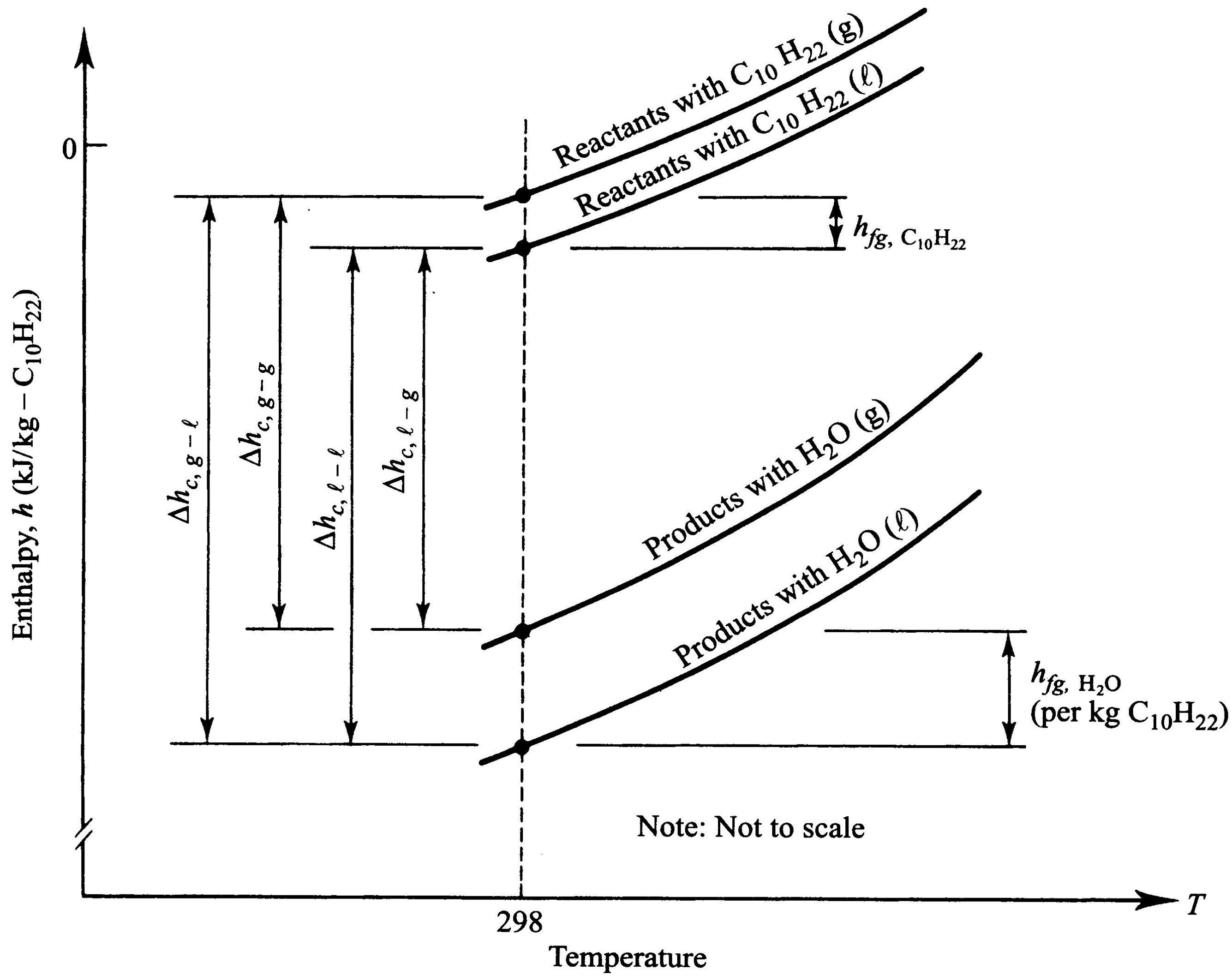

Figure 2.9 Enthalpy–temperature plot illustrating calculation of heating values in Example 2.4.

Example 2.4

A. Determine the upper and lower heating values at 298 K of gaseous n-decane, $C_{10}H_{22}$, per kilomole of fuel and per kilogram of fuel. The molecular weight of n-decane is 142.284.

B. If the enthalpy of vaporization of n-decane is 359 kJ/kg$_{\text{fuel}}$ at 298 K, what are the upper and lower heating values of liquid n-decane?

Solution

A. For 1 mole of $C_{10}H_{22}$, the combustion equation can be written as

$$C_{10}H_{22}(g) + 15.5(O_2 + 3.76N_2) \rightarrow 10CO_2 + 11H_2O(1 \text{ or } g) + 15.5(3.76)N_2.$$

For either the upper or lower heating value,

$$\Delta H_c = -\Delta H_R = H_{\text{reac}} - H_{\text{prod}},$$

where the numerical value of H_{prod} depends on whether the H_2O in the products is liquid (determining higher heating value) or gaseous (determining lower heating value). The sensible enthalpies for all species involved are zero since we desire ΔH_c at the reference state (298 K). Furthermore, the enthalpies of formation of the O_2 and N_2 are also zero at 298 K. Recognizing that

$$H_{\text{reac}} = \sum_{\text{reac}} N_i \bar{h}_i \qquad \text{and} \qquad H_{\text{prod}} = \sum_{\text{prod}} N_i \bar{h}_i,$$

we obtain

$$\Delta H_{c,H_2O(l)} = \text{HHV} = (1)\bar{h}^o_{f,C_{10}H_{22}} - \left[10\bar{h}^o_{f,CO_2} + 11\bar{h}^o_{f,H_2O(l)}\right].$$

Table A.6 (Appendix A) gives the enthalpy of formation for gaseous water and the enthalpy of vaporization. With these values, we can calculate the enthalpy of formation for the liquid water (Eqn. 2.18):

$$\bar{h}^o_{f,H_2O(l)} = \bar{h}^o_{f,H_2O(g)} - \bar{h}_{fg} = -241{,}847 - 44{,}010 = -285{,}857 \text{ kJ/kmol}.$$

Using this value, together with enthalpies of formation given in Appendices A and B, we obtain the higher heating value:

$$\Delta H_{c,\mathrm{H_2O,(l)}} = (1)\left(-249{,}659\ \frac{\mathrm{kJ}}{\mathrm{kmol}}\right) - \left[10\left(-393{,}546\ \frac{\mathrm{kJ}}{\mathrm{kmol}}\right) + 11\left(-285{,}857\ \frac{\mathrm{kJ}}{\mathrm{kmol}}\right)\right] = 6{,}830{,}096\ \mathrm{kJ}$$

and

$$\boxed{\Delta \bar{h}_c = \frac{\Delta H_c}{N_{\mathrm{C_{10}H_{22}}}} = \frac{6{,}830{,}096\ \mathrm{kJ}}{1\ \mathrm{kmol}} = 6{,}830{,}096\ \mathrm{kJ/kmol_{C_{10}H_{22}}}}$$

or

$$\boxed{\Delta h_c = \frac{\Delta \bar{h}_c}{MW_{C_{10}H_{22}}} = \frac{6{,}830{,}096\ \frac{\mathrm{kJ}}{\mathrm{kmol}}}{142.284\ \frac{\mathrm{kg}}{\mathrm{kmol}}} = 48{,}003\ \mathrm{kJ/kg_{C_{10}H_{22}}}}$$

For the lower heating value, we use $\bar{h}^o_{f,\mathrm{H_2O(g)}} = -241{,}847\ \mathrm{kJ/kmol}$ in place of $\bar{h}^o_{f,\mathrm{H_2O(l)}} = -285{,}857\ \mathrm{kJ/kmol}$. Thus,

$$\boxed{\Delta \bar{h}_c = 6{,}345{,}986\ \mathrm{kJ/kmol_{C_{10}H_{22}}}}$$

or

$$\boxed{\Delta h_c = 44{,}601\ \mathrm{kJ/kg_{C_{10}H_{22}}}}$$

B. For $C_{10}H_{22}$, in the liquid state,

$$H_{\text{reac}} = (1)\left(\bar{h}^o_{f,C_{10}H_{22}(g)} - \bar{h}_{fg}\right),$$

or

$$\Delta h_c\begin{pmatrix}\text{liquid}\\ \text{fuel}\end{pmatrix} = \Delta h_c\begin{pmatrix}\text{gaseous}\\ \text{fuel}\end{pmatrix} - h_{fg}.$$

Thus,

$$\boxed{\begin{aligned}\Delta h_c\ (\text{higher}) &= 48{,}003 - 359\\ &= 47{,}644\ \text{kJ/kg}_{C_{10}H_{22}}\\ \Delta h_c\ (\text{lower}) &= 44{,}601 - 359\\ &= 44{,}242\ \text{kJ/kg}_{C_{10}H_{22}}\end{aligned}}$$