CEN 202 THERMODYNAMICS

CHAPTER 4. HEAT EFFECTS

TEXT BOOK: : J. M. SMITH, H. C. VAN NESS, M. M. ABBOTT, M. T. SWIHART. "INTRODUCTION TO CHEMICAL ENGINEERING THERMODYNAMICS", EIGHTH EDITION. 2018

EVALUATION OF THE SENSIBLE-HEAT INTEGRAL

Evaluation of the integral $\int C_P\,dT$ is accomplished by substitution for C_P as a function of T. For temperature limits of T_0 and T the result is:

$$\int_{T_0}^{T} \frac{C_P}{R}\,dT = A(T - T_0) + \frac{B}{2}\left(T^2 - T_0^2\right) + \frac{C}{3}\left(T^3 - T_0^3\right) + D\left(\frac{T - T_0}{TT_0}\right)$$

Factoring $(T-T_0)$ from each term on the right side of the equation (above) gives:

$$\int_{T_0}^{T} \frac{C_P}{R}\,dT = \underbrace{\left[A + \frac{B}{2}(T + T_0) + \frac{C}{3}\left(T^2 - T_0^2 + TT_0\right) + \frac{D}{TT_0}\right]}_{\frac{\langle C_P \rangle_H}{R}}(T - T_0)$$

We identify the quantity in square brackets as $\langle C_P \rangle_H / R$, where $\langle C_P \rangle_H$ is defined as a mean heat capacity for the temperature range from T_0 to T.

STANDARD HEAT OF REACTION

Heat effects of chemical processes are important for chemical reactions which are accompanied by the transfer of heat, by temperature changes during reaction, or by both.

Heat of reaction: Fuel + air (at T)→ combustion chamber (reaction occurs)→ combustion products → cooled at T (using a water-jacket).

From the overall energy balance (no shaft work, potential and kinetic energy changes): $\Delta H = Q$

Thus the enthalpy change caused by the combustion reaction is equal in magnitude to the heat flowing from the reaction products to the water, and may be calculated from the temperature rise and flow rate of the water. The enthalpy change of reaction ΔH is called the heat of reaction. If the reactants and products are in their standard states, then the heat effect is the standard heat of reaction.

STANDARD HEAT OF FORMATION

A formation reaction is defined as a reaction that forms a single compound from its constituent elements. For example, the reaction $C + 1/2O_2 + 2H_2 \rightarrow CH_3OH$ is a formation reaction for methanol.

The reaction $H_2O + SO_3 \rightarrow H_2SO_4$ is not a formation reaction, because it forms sulphuric acid not from the elements but from other compounds. Formation reactions are understood to produce 1 mol of product; the heat of formation is therefore based on 1 mol of the compound formed.

At 298.15 K, The standard heat of formation of a compound at this temperature is represented by the **symbol ΔH°_{f298}**. The degree symbol (°) denotes the standard-state value, Subscript (f) identifies a heat of formation,

The 298 is the rounded absolute temperature in kelvins.

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STANDARD HEAT OF COMBUSTION

Only a few formation reactions can actually be carried out at the conditions of interest, and therefore data for these reactions are determined indirectly. One kind of reaction that readily lends itself to experiment is the combustion reaction, and many standard heats of formation come from standard heats of combustion, measured calorimetrically.

The value for liquid water product is called the higher heat of combustion, while that with water vapour as product is the lower heat of combustion. Data are always based on 1 mol of the substance burned.

A reaction such as the formation of n-butane:

$$4C(s) + 5H_2(g) \rightarrow C_4H_{10}(g)$$

is not feasible in practice. However, this equation results from combination of the following combustion reactions:

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STANDARD HEAT OF COMBUSTION

$4C(s) + 4O_2(g) \rightarrow 4CO_2(g)$	$\Delta H^\circ_{298} = (4)(-393{,}509)$
$5H_2(g) + 5/2O_2(g) \rightarrow 5H_2O(l)$	$\Delta H^\circ_{298} = (5)(-285{,}830)$
$4CO_2(g) + 5H_2O(l) \rightarrow C_4H_{10}(g) + 13/2O_2(g)$	$\Delta H^\circ_{298} = 2{,}877{,}396$
$4C(s) + 5H_2(g) \rightarrow C_4H_{10}(g)$	**$\Delta H^\circ_{298} = -125{,}790$ J**

This result is the standard heat of formation of n-butane listed in Table C.4 of App. C.

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