

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

CEN 202 THERMODYNAMICS, HEAT EFFECTS

Heat effects refer to physical and chemical phenomena that are associated with heat transfer to or from a system or that result in temperature changes within a system, or both.

Latent heat: Latent heat is related to changes in phase between liquids, gases, and solids (at constant T and P).

Chemical reactions are characterised by heats of reaction (combustion reactions evolve heat, for example). Every chemical or biochemical process is associated with one or more heat effects.

SENSIBLE HEAT EFFECTS

- Heat transfer to or from a system in which there are no phase transitions, no chemical reactions, and no changes in composition causes a "sensible heat effect", i.e., the temperature of the system is caused to change.
- Briefly, **sensible heat** is related to changes in temperature of a gas or object with no change in phase.
- A relation between; the quantity of heat transferred \leftrightarrow the resulting temperature change.

SENSIBLE HEAT EFFECTS

- **U (molar or specific) = U (T, V).** Then,

$$\bullet \quad dU = \underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\bullet \quad dU = C_V dT + \underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{=0} dV$$

- For any closed-system constant-volume process.
- Whenever the internal energy is independent of volume, as for the ideal-gas state and the incompressible liquid.

- In either case, **$dU = C_V dT$ and $\Delta U = \int_{T_1}^{T_2} C_V dT$**

SENSIBLE HEAT EFFECTS

- For enthalpy;
- H (molar or specific) = $H(T, P)$. Then,

$$dH = \underbrace{\left(\frac{\partial H}{\partial T}\right)_P}_{C_P} dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$dH = C_P dT + \underbrace{\left(\frac{\partial H}{\partial P}\right)_T}_{=0} dP$$

The final term is zero in two circumstances:

- For any constant-pressure process.
- When the enthalpy is independent of pressure, regardless of process. This is exactly true for the ideal-gas state and approximately true for real gases at low pressure and high temperature.
- In either case, $dH = C_P dT$ and $\Delta H = \int_{T_1}^{T_2} C_P dT$

TEMPERATURE DEPENDENCE OF THE HEAT CAPACITY

- Evaluation of the integral in Eq. $Q = \Delta H = \int_{T_1}^{T_2} C_P dT$ requires knowledge of the temperature dependence of the heat capacity. This is usually given by an empirical equation; the **two simplest expressions** of practical value are:

$$\frac{C_P}{R} = \alpha + \beta T + \gamma T^2 \text{ and } \frac{C_P}{R} = a + bT + cT^{-2}$$

where α , β , and γ and a , b , and c are constants characteristic of the particular substance. With the exception of the last term, these equations are of the same form. We therefore combine them to provide a single expression:

$$\frac{C_P}{R} = A + BT + CT^2 + DT^{-2}$$

where either C or D is usually zero, depending on the substance considered. Because the ratio C_P/R is dimensionless, the units of C_P are governed by the choice of R . The parameters are independent of temperature, but, at least in principle, depend on the value of the constant pressure.

HEAT CAPACITY IN THE IDEAL-GAS STATE

Temperature dependence is expressed analytically (for ideal gas):

$$\frac{C_P^{ig}}{R} = A + BT + CT^2 + DT^{-2}$$

Values of the constants are given in Tables (Table C.1 of App. C for a number of common organic and inorganic gases) in available literature.

The two ideal-gas-state heat capacities are related: (remember: $C_p = C_v + R$)

$$\frac{C_V^{ig}}{R} = \frac{C_P^{ig}}{R} - 1$$

The temperature dependence of $\frac{C_V^{ig}}{R}$ follows from the temperature dependence of $\frac{C_P^{ig}}{R}$.