CEN 202 Thermodynamics

Introduction to Chemical Engineering Thermodynamics

CHAPTER 2

The Reversible Process

A process is reversible when its direction can be reversed at any point by an infinitesimal change in external conditions.

The reversible process is ideal in that it produces a best possible result: it yields the minimum work input required or maximum work output attainable from a specified process. It represents a limit to the performance of an actual process that is never fully realised.

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CHAPTER 2: The Reversible Process

Summary Remarks on Reversible Processes

A reversible process:

- Can be reversed at any point by an infinitesimal change in external conditions
- Is never more than minutely removed from equilibrium
- Traverses a succession of equilibrium states
- Is frictionless
- Is driven by forces whose imbalance is infinitesimal in magnitude
- Proceeds infinetely slowly
- When reversed, retraces its path, restoring the initial state of system and surroundings.

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CHAPTER 2: The Reversible Process

Computing Work for Reversible Processes

As reported above, work is obtained as results of expansion or compression process in cylinder:

$$dW = -P\, dV^t \qquad (1.3)$$

For mechanically reversible expansion or compression of a fluid in a piston/cylinder process, the equation may be integrated:

$$W = -\int_{V_1^t}^{V_1^2} P dV^t$$

To find the work of an irreversible process for the same change in Vt, one needs an efficiency, which relates the actual work to the reversible work.

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CHAPTER 2: Closed-System Reversible Processes: Enthalpy

For 1 mole of a homogenous fluid contained in a closed system, the energy balance is written;

$$dU = dQ + \underbrace{dW}_{-PdV}$$

$$dU = dQ - PdV$$

(the general energy balance, mechanically reversible process)

$dU = dQ$ Integration yields $\Delta U = Q$ ***(const V)***

For a constant-pressure change of state:

$$dU + PdV = d(U + PV) = dQ$$

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CHAPTER 2: Closed-System Reversible Processes: Enthalpy

The group $U + PV$ naturally arises here and in many other applications. This is a new thermodynamic property which is mathematical definition of enthalpy:

$$\boldsymbol{H \equiv U + PV} \qquad (2.10)$$

where H, U and V are molar or unit-mass value.

$\boldsymbol{dH = dQ}$ Integration yields $\Delta H = Q$ (const P) (mechanically reversible process)

The differential form of Eq. (2.10) is:

$dH = dU + d(PV)$ integration of the equation;

$$\Delta H = \Delta U + \Delta(PV)$$