# CH365 Chemical Engineering Thermodynamics

Lesson 23
Calculation of Entropy and
Entropy Changes for an Ideal Gas

# Summary of Section 5.4

There exists a property called entropy S, which is an intrinsic property of a system, functionally related to the measurable coordinates characterizing the system.  For a reversible process, changes in this property are given by Eq. 5.1.

$$dS^t = \frac{dQ_{rev}}{T} \qquad \text{Eq. 5.1} \qquad \text{(Axiom to 2}^{nd}\text{ Law)}$$

The change in entropy for any system undergoing a finite reversible process is:

$$\Delta S^t = \int \frac{dQ_{rev}}{T} \qquad \text{Integral of Eq. 5.1}$$

When a system undergoes an irreversible process between two equilibrium states, the irreversible path cannot be directly integrated.  The entropy change of the system is evaluated by integrating Eq. 5.1 along an arbitrarily chosen reversible process that accomplishes the same change of state as the actual process.  Because entropy is a state function, the entropy changes of the irreversible and reversible processes are identical.

# Independent of Path – State Function

$$dS^t = \frac{dQ_{rev}}{T}$$

reversible process

$D$

$B$

irreversible process

$P$

$A$

reversible process

$C$

$V^t$
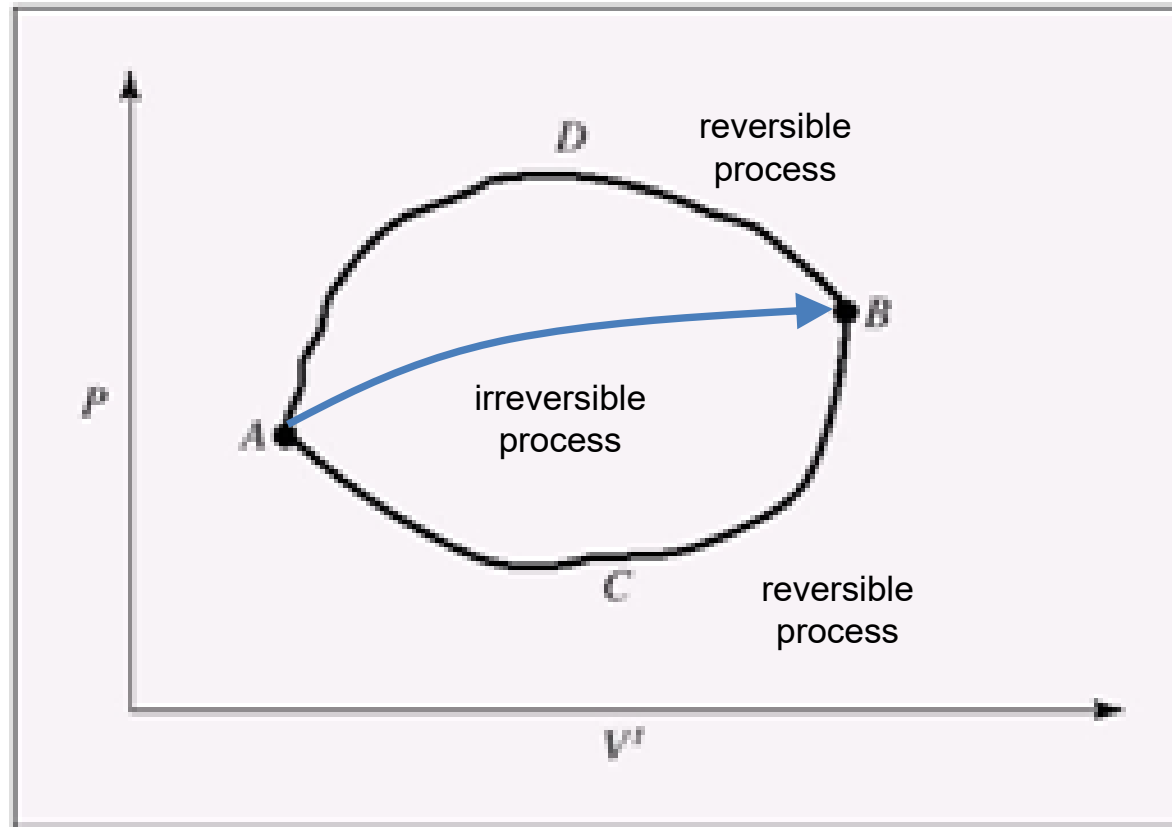
$$\Delta S^t_{ACB} = \int_{ACB} \frac{dQ_{rev}}{T}$$

$$\Delta S^t_{ADB} = \int_{ADB} \frac{dQ_{rev}}{T}$$

$$\Delta S^t_{AB} = \Delta S^t_{ACB} = \Delta S^t_{ADB}$$

true for <u>irreversible</u> processes as well as reversible

# Entropy Changes for an Ideal Gas

$$dU = dQ_{rev} - PdV \qquad \text{First Law, Eq. 2.7, reversible}$$

$$H = U + PV \qquad \text{Definition of enthalpy, Eq. 2.10}$$

$$dH = dU + PdV + VdP \qquad \text{Differentiate}$$

$$dH = dQ_{rev} - PdV + PdV + VdP \quad = dQ_{rev} + VdP$$

$$dQ_{rev} = dH - VdP \qquad dH = C_P^{ig} dT \quad \text{and} \quad V = \frac{R \cdot T}{P}$$

$$dQ_{rev} = C_P^{ig} \cdot dT - R \cdot T \cdot \frac{dP}{P}$$

$$\frac{dQ_{rev}}{T} = C_P^{ig} \frac{dT}{T} - R \cdot \frac{dP}{P} \qquad dS = \frac{dQ_{rev}}{T} \qquad \text{Eq. 5.1}$$

$$dS = C_P^{ig} \frac{dT}{T} - R \cdot \frac{dP}{P}$$

$$\frac{dS}{R} = \frac{C_P^{ig}}{R} \frac{dT}{T} - d \ln P \quad \Longleftrightarrow \quad \frac{\Delta S}{R} = \int_{T_0}^{T} \frac{C_P^{ig}}{R} \frac{dT}{T} - \ln \frac{P}{P_0} \qquad \text{Eq. 5.10}$$

# Integrated Forms

$$\text{ICPS} = \int_{T_0}^{T} \frac{C_P^{ig}}{R} \frac{dT}{T} = A \cdot \ln\frac{T}{T_0} + \left[ B + \left( C + \frac{D}{T_0^2 T^2} \right) \cdot \left( \frac{T+T_0}{2} \right) \right] \cdot (T - T_0)$$

Eq. 5.11

$$\text{MCPS} = \frac{\left\langle C_P^{ig} \right\rangle_S}{R} = A + \left[ B + \left( C + \frac{D}{T_0^2 T^2} \right) \cdot \left( \frac{T+T_0}{2} \right) \right] \cdot \left( \frac{T-T_0}{\ln(T/T_0)} \right)$$

Eq. 5.13

$$\text{where} \quad \left\langle C_P^{ig} \right\rangle_S = \frac{\int_{T_0}^{T} C_P^{ig} dT / T}{\ln(T/T_0)}$$

Eq. 5.12

$$\frac{\Delta S}{R} = \int_{T_0}^{T} \frac{C_P^{ig}}{R} \frac{dT}{T} - \ln\frac{P}{P_0}$$

Eq. 5.10

$$\frac{\Delta S}{R} = \text{ICPS} - \ln\frac{P}{P_0}$$

$$\frac{\Delta S}{R} = \text{MCPS} \cdot \ln\left( \frac{T}{T_0} \right) - \ln\frac{P}{P_0}$$

Eq. 5.14

# Example 5.3

Methane gas at 550 K and 5 bar undergoes a reversible adiabatic expansion to 1 bar. Assuming methane to be an ideal gas at these conditions, find its final temperature.

# Homework

# Problem 5.8

With respect to 1 kg of liquid water:

(a) Initially at 0 deg C, it is heated to 100 deg C by contact with a heat reservoir at 100 deg C.  What is the entropy change of the water?  What is the entropy change of the heat reservoir?  What is $\Delta S_{total}$?

(b) Initially at 0 deg C, it is first heated to 50 deg C by contact with a heat reservoir at 50 deg C, and then heated to 100 deg C by contact with a heat reservoir at 100 deg C.  What is $\Delta S_{total}$?

(c) Explain how the water might be heated from 0 deg C to 100 deg C so that $\Delta S_{total} = 0$.

$$C_{P,water} = 4.184 \frac{kJ}{kg \cdot C} = 4.184 \frac{kJ}{kg \cdot K}$$

# Problem 5.10

An ideal gas, CP = (7/2)R, is heated in a steady-flow heat exchanger from 70 deg C to 190 deg C by another stream of the same gas, which enters at 320 deg C. The flow rates of the two streams are the same, and heat losses from the exchanger are negligible.

(a) Calculate the molar entropy changes of the two gas streams for both parallel and countercurrent flow in the exchanger.

(b) What is $\Delta S_{total}$ in each case?

(c) Repeat parts (a) and (b) for countercurrent flow if the heating stream enters at 200 deg C.

Assume pressure drop is negligible. Not a good assumption but needed.