# Entropy Change

- Property diagrams (T-s and h-s diagrams) from the definition of the entropy, it is known that  $\delta Q=TdS$  during a reversible process. The total heat transfer during this process is given by  $Q_{reversible} = \int TdS$
- Therefore, it is useful to consider the T-S diagram for a reversible process involving heat transfer



• On a T-S diagram, the area under the process curve represents the heat transfer for a reversible process

• Show the Carnot cycle on a T-S diagram and identify the heat transfer at both the high and low temperatures, and the work output from the cycle.



• 1-2, reversible isothermal heat transfer  $Q_H = \int TdS = T_H(S_2-S_1)$  area 1-2-B-A • 2-3, reversible, adiabatic expansion isentropic process, S=constant (S<sub>2</sub>=S<sub>3</sub>) • 3-4, reversible isothermal heat transfer  $Q_L = \int TdS = T_L(S_4-S_3)$ , area 3-4-A-B • 4-1, reversible, adiabatic compression isentropic process, S<sub>1</sub>=S<sub>4</sub>

• Net work  $W_{net} = Q_H - Q_L$ , the area enclosed by 1-2-3-4, the shaded area

# Mollier Diagram

- Enthalpy-entropy diagram, h-s diagram: it is valuable in analyzing steady-flow devices such as turbines, compressors, etc.
- Δh: change of enthalpy from energy balance (from the first law of thermodynamics)
- $\Delta$ s: change of entropy from the second law ( a measure of the irreversibilities during an adiabatic process)



# **TdS Equations**

• For a closed system containing a pure compressible substance undergoing a reversible process

 $dU = \delta Q_{rev} - \delta W_{rev} = TdS - PdV$ 

TdS = dU + PdV, or Tds = du + pdv (per unit mass)

> This is the famous Gibbsian equation

- Eliminate du by using the definition of enthalpy h=u+pv dh = du + pdv + vdp, thus du + pdv = dh - vdp Tds = du + pdv, also Tds = dh - vdp
- Important: these equations relate the entropy change of a system to the changes in other properties: dh, du, dp, dv. Therefore, they are independent of the processes. These relations can be used for reversible as well as irreversible processes. (Even their derivation is based on a reversible process.)

• Consider steam is undergoing a phase transition from liquid to vapor at a constant temperature of 20°C. Determine the entropy change  $s_{fg}=s_g-s_f$  using the Gibbsian equations and compare the value to that read directly from the thermodynamic table.

 $ds = \frac{du}{T} + \frac{P}{T} dv$ , change from liquid to vapor

$$s_{fg} = s_g - s_f = \frac{1}{T}(u_g - u_f) + \frac{P}{T}(v_g - v_f)$$

From table A-4, T=20°C, P=0.002338 MPa,  $v_f$ =0.001002(m<sup>3</sup>/kg),  $v_g$ =57.79(m3/kg),  $u_f$ =83.9(kJ/kg),  $u_g$ =2402.9(kJ/kg)  $s_{fg}$ =(1/293)(2402.9-83.9)+(2.338/293)(57.79-0.001002)=8.375(kJ/kg K) It compares favorably with the tabulated value  $s_{fg}$ =8.3715(kJ/kg K) Entropy change of an incompressible substance

• For most liquids and all solids, the density is not changed as pressure changes, that is, dv=0. Gibbsian equation states that Tds=du+pdv=du, du=CdT, for an incompressible substance  $C_p=C_v=C$  is a function of temperature only. Therefore, ds=du/T=CdT/T

Integrate to determine the entropy change during a process

$$s_2 - s_1 = \int_{1}^{2} ds = \int_{1}^{2} C(T) \frac{dT}{T} \cong C_{avg} \ln(\frac{T_2}{T_1})$$

where  $C_{avg}$  is the averaged specific heat of the substance over the given temperature range

• Specific heats for some common liquids and solids can be found in thermodynamic tables such as Table A-14 to A-19

An 1-kg metal bar initially at 1000 K is removed from an oven and quenched by immersing in a closed tank containing 20 kg of water initially at 300 K. Assume both substances are incompressible and c(water)=4(kJ/kg K), c(metal)=0.4(kJ/kg K). Neglect heat transfer between the tank and its surroundings. (a) Determine the final temperature of the metal bar, (b) entropy generation during the process.



### Solution

(a) Energy balance from the first law:

 $\Delta U = Q - W = 0$ , no heat transfer and no work done

 $\Delta U_{\text{water}} + \Delta U_{\text{metal bar}} = 0, \text{ both bar and water reach final temperature } T_{\text{f}}$  $m_{w}c_{w}(T_{f} - T_{w}) + m_{m}c_{m}(T_{m} - T_{f}) = 0$  $T_{f} = \frac{m_{w}(c_{w}/c_{m})T_{w} + m_{m}T_{m}}{m_{w}(c_{w}/c_{m}) + m_{m}} = \frac{(20)(10)(300) + (1)(1000)}{(20)(10) + 1} = 303.5(K)$ 

(b) No heat transfer with the outside Q = 0, the entropy balance of the system  $\Delta s = s(\text{generation}) = s_g$ 

$$s_g = \Delta s(\text{water}) + \Delta s(\text{bar}) = m_w c_w \ln \frac{T_f}{T_w} + m_m c_m \ln \frac{T_f}{T_m}$$

$$s_g = (20)(4) \ln \frac{303.5}{300} + (1)(0.4) \ln \frac{303.5}{1000} = 0.928 - 0.477 = 0.451(kJ / K)$$

The total entropy of the system increases, thus satisfy the second law

Entropy change of an ideal gas

• From the Gibbsian equations, the change of entropy of an ideal gas can be expressed as

$$ds = \frac{du}{T} + \frac{P}{T}dv = \frac{dh}{T} - \frac{v}{T}dP$$

For an ideal gas, u=u(T) and h=h(T),  $du=c_v(T)dT$  and  $dh=c_p(T)dT$ and Pv=RT

$$ds = c_v(T)\frac{dT}{T} + R\frac{dv}{v}$$
, and  $ds = c_P(T)\frac{dT}{T} - R\frac{dP}{P}$ 

By integration, the change of the entropy is

$$s_2 - s_1 = \int_{1}^{2} c_v(T) \frac{dT}{T} + R \ln(\frac{v_2}{v_1}) \text{ or } s_2 - s_1 = \int_{1}^{2} c_P(T) \frac{dT}{T} - R \ln(\frac{P_2}{P_1})$$

we need to know the function  $c_p(T)$  and  $c_v(T)$  in order to complete the integration,

#### Cases with constant specific heats

• When specific heats are constant, the integration can be simplified:

$$s_{2} - s_{1} = c_{v} \ln(\frac{T_{2}}{T_{1}}) + R \ln(\frac{v_{2}}{v_{1}}) \text{ or}$$
$$s_{2} - s_{1} = c_{P} \ln(\frac{T_{2}}{T_{1}}) - R \ln(\frac{P_{2}}{P_{1}})$$

• If a process is isentropic (that is adiabatic and reversible), ds=0,  $s_1=s_2$ , then it can be shown that

$$\frac{T_2}{T_1} = (\frac{v_1}{v_2})^{k-1}, \text{ and } \frac{T_2}{T_1} = (\frac{P_2}{P_1})^{(k-1)/k}$$
  
and  $\frac{P_2}{P_1} = (\frac{v_1}{v_2})^k$ , where  $k = \frac{c_p}{c_v}$ 

• Air is compressed from an initial state of 100 kPa and 300 K to 500 kPa and 360 K. Determine the entropy change using constant  $c_p=1.003$  (kJ/kg K)

$$s_2 - s_1 = c_P \ln(\frac{T_2}{T_1}) - R \ln(\frac{P_2}{P_1})$$
 if  $c_P$  is constant  
 $s_2 - s_1 = 1.003 \ln \frac{360}{300} - (0.287) \ln \frac{500}{100} = -0.279 (kJ / kg K)$ 

• Negative entropy due to heat loss to the surroundings