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Gibb's Equation

- For simple compressible substance (nonreacting) we have $S = S(U,V)$
- Thus $$dS = \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV$$
- From *p*, *T* def'ns.

$$\boxed{dS = \frac{1}{T}dU + \frac{p}{T}dV}$$

Gibb's Eq.
can determine S from measureable quantities

- also $$dU = TdS - pdV$$

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Example: Gas Diffusion (Mixing)

U_A	U_B
V	V
T	T
A	B

- Two gases initially separated in equal volumes that are then allowed to mix
- What is S_C (total) when system reaches equilibrium (uniformly mixed)?
- Assuming inert perfect gases $S_C = S_A(U_A,V_A) + S_B(U_B,V_B)$
- Gibbs for A:

$$dS_A = \left(\frac{dU}{T}\right)_A + \left(\frac{p}{T}dV\right)_A = \left(\frac{dU}{T}\right)_A + \left(\frac{pV}{T}\frac{dV}{V}\right)_A$$

$$= \left(\frac{dU}{T}\right)_A + \left(Nk\frac{dV}{V}\right)_A$$

\# molec.

- Gibbs for B:

$$dS_B = \left(\frac{dU}{T}\right)_B + \left(Nk\frac{dV}{V}\right)_B$$

Example: Gas Diffusion (Mixing)

A	B
U_A	U_B
V	V
T	T

- Combine

$$dS_C = dS_A + dS_B = \overbrace{\frac{dU_A}{T} + \frac{dU_B}{T}}^{\text{0, isolated}} + k\left(N_A\frac{dV_A}{V_A} + N_B\frac{dV_B}{V_B}\right)$$

$$\Delta S_C = k\left(N_A + N_B\right)\ln\frac{2V}{V}$$

$$\boxed{\Delta S_C = k\left(N_A + N_B\right)\ln 2}$$

entropy PRODUCED with
no change in p or T of system (C)

Heat Transfer and Entropy Transfer

- Consider **T**hermal **E**nergy **R**eservoir (TER)
  - CM with fixed volume, only exchanges energy as Q, uniform and constant internal T
  - always in equil.

TER
T, dU

$\uparrow$ δQ

- Since fixed volume, Gibbs $\Rightarrow$ $dS = \frac{1}{T}dU$
- 1st Law $\Rightarrow$ $dU = \delta Q$
- Combine

$$dS = \frac{\delta Q}{T}$$

heat transfer can cause
entropy change

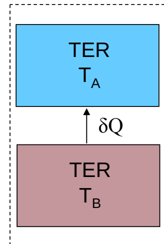
- since TER always in equil.
  heat transfer $\Rightarrow$ entropy transfer

Entropy Production

- Now consider two interacting TERs at two T's, which form isolated system
- From previous result

$$dS_A = \frac{-\delta Q}{T_A} \qquad dS_B = \frac{+\delta Q}{T_B}$$

$$dS_B = -\left(\frac{T_A}{T_B}\right) dS_A$$



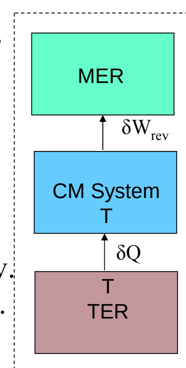
- Since overall system isolated $dS_C = \delta \mathcal{P}_s \geq 0$

$$dS_A\left(1 - \frac{T_A}{T_B}\right) \geq 0 \qquad \text{if } T_B > T_A \text{ then } dS_A > 0$$

  - entropy production associated with Q across finite temperature difference

Second Law for Control Mass

- Consider CM interacting with a TER and a **M**echanical **E**nergy **R**eservoir (MER)
  - CM with no microscopic disorder (no entropy), can only exchange energy as reversible work
- Together they form isolated system



2nd Law $\delta \mathcal{P}_s = d\left(S_{TER} + \overset{0}{\cancel{S_{MER}}} + S_{CM}\right)$

$$= -\delta Q / T + dS_{CM}$$

$$\boxed{dS_{CM} = \underbrace{\delta Q / T}_{S \text{ xfer}} + \underbrace{\delta \mathcal{P}_s}_{S \text{ prod.}}} \qquad dS_{CM} \begin{cases} > \delta Q / T & \text{irrev.} \\ = \delta Q / T & \text{rev.} \end{cases}$$

inequality

$$\Delta S_{CM} = \int_1^2 \frac{\delta Q}{T} + \mathcal{P}_s$$

adiab.+rev.
one way to get isentropic

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Availability Analysis

Second Law-18

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Carnot Efficiency

Second Law-19

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