

## Lecture 5

- Statistical interpretation of entropy
  - Boltzmann entropy
  - Application to ideal gas
- Probabilistic interpretation of second law
- Entropy balance for open system
- Calculating reversible work by combining first and second laws
- Combined first and second laws for simple system, reversible process

Read Chs. 4 and 5 Callen

# Objectives

- Know the Boltzmann entropy
- Understand the probabilistic interpretation of second law
- Know open system entropy balance and 2<sup>nd</sup> law
- Use combined 1<sup>st</sup> and 2<sup>nd</sup> law to solve for reversible work problems
- Understand and memorize combined 1<sup>st</sup> and 2<sup>nd</sup> law for simple systems, reversible process
- Understand the meaning of this equation (e.g., meaning of the differential symbol d)

# Boltzmann Entropy

$$S = k \ln \Omega$$

(ca. 1872)

$\Omega$ : total number of microstates (at specified volume, number of particles, and energy)

*Usually* associated with disorder

$k=R/N_a=1.38\times 10^{-23}$  (J/K) Boltzmann constant



Ludwig Boltzmann 1844-1906

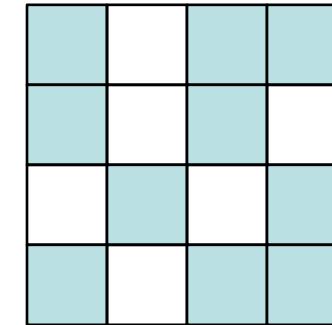
W: Wahrscheinlichkeit

# Lattice Gas/Lattice Model for Liquid Mixture

$M$  lattice cells filled with  $N$  identical objects

Single occupancy

$M$  lattice cells filled with  $N$  identical objects of type A,  $M-N$  objects of type B



$$\Omega = \frac{M!}{N! (M - N)!}$$

$$S = \ln \frac{M!}{N! (M - N)!} = \ln M! - \ln N! - \ln(M - N)!$$

## Sterling's Approximation

$$\ln n! \approx n \ln n - n$$

Proof:

1. Elementary:

$$\ln n! = \sum_{j=1}^n \ln j \approx \int_1^n \ln x \, dx = n \ln n - n + 1 \approx n \ln n - n$$

2. Asymptotic limit of Gamma function:

$$n! = \Gamma(n+1) = \int_0^\infty x^n e^{-x} dx \approx \sqrt{2\pi n} \left(\frac{n}{e}\right)^n$$

## Lattice Gas/Lattice Model for Liquid Mixture

$$S/k = \ln M! - \ln N! - \ln(-N)!$$

$$= M \ln M - M - N \ln N + N - (M - N) \ln(M - N) + M - N$$

$$S = kM \ln M - kN \ln N - k(M - N) \ln(M - N)$$

$$S = kM [x \ln x + (1 - x) \ln(1 - x)]$$

Ideal mixing

## Application to Ideal Gas

Configuration part for putting  $N$  molecules into  $\frac{V}{\Lambda^3}$  cells allowing multi occupancy

$$\Omega_{conf} = \frac{1}{N!} \left( \frac{V}{\Lambda^3} \right)^N \quad \Lambda = \left( \frac{h^2}{2\pi mkT} \right)^{1/2}$$

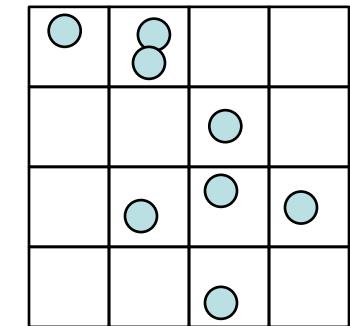
de Broglie  
thermal  
wavelength

$$S_{conf} = -Nk \left[ \ln \frac{N\Lambda^3}{V} - 1 \right]$$

$$\Delta S_{conf} = Nk \ln \frac{V_2}{V_1} = nR \ln \frac{V_2}{V_1}$$

$$\text{For } V_2 = 2V, V_1 = 2V$$

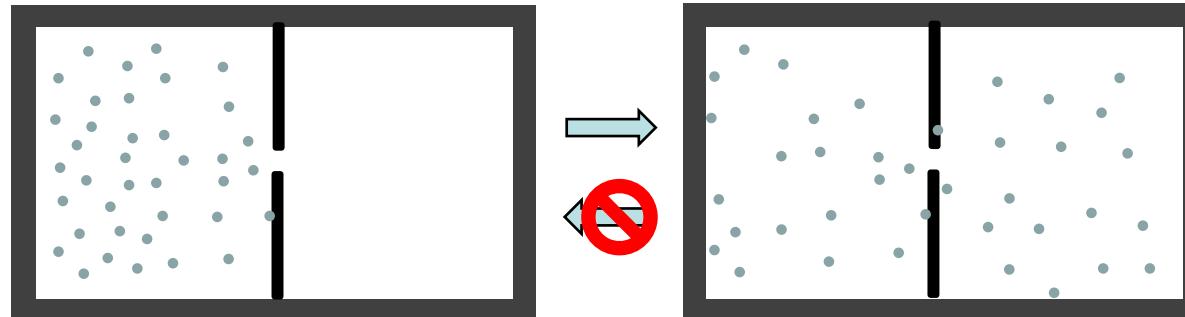
$$\Delta S_{conf} = Nk \ln \frac{V_2}{V_1} = nR \ln 2$$



# Probabilistic Interpretation of Entropy Change

forward       $\Delta S = S(2V) - S(V) = k \ln \frac{\Omega(2V)}{\Omega(V)} = kN \ln 2$

backward     $S(V) - S(2V) = k \ln \frac{\Omega(V)}{\Omega(2V)} = -kN \ln 2$



Probability that the gas molecules will spontaneously collect into left half:

$$\Pr(V|2V) = \exp \frac{S(V) - S(2V)}{k} = \exp(-N \ln 2) = \left(\frac{1}{2}\right)^N$$

practically zero for  $N \sim 10^{23}$

## Probabilistic Interpretation of Second Law

A process that is deemed impossible due to violation of the second law is one that happens with a vanishingly small probability

Example: uneven partitioning of gas into two equal volumes

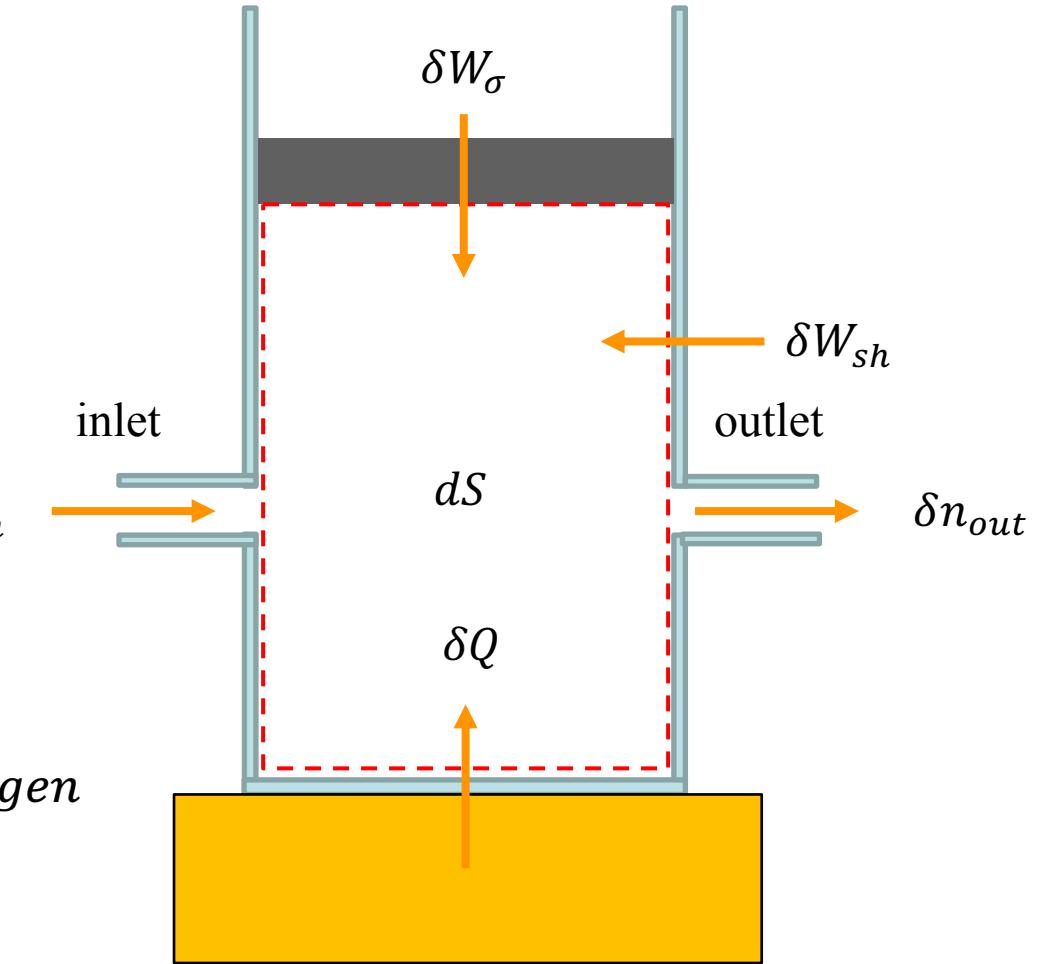
# Entropy Balance for Open Systems

For a control volume:

$$dS = s_{in}\delta n_{in} - s_{out}\delta n_{out} + \frac{\delta Q}{T_{res}} + dS_{gen}$$

Can generalize to multi heat baths:

$$dS = s_{in}\delta n_{in} - s_{out}\delta n_{out} + \sum_i \frac{\delta Q_i}{T_{res,i}} + dS_{gen}$$



## Reversible Work from Combined Energy and Entropy Balance

$$dU = h_{in}\delta n_{in} - h_{out}\delta n_{out} + \delta Q + \delta W_s + \delta W_\sigma$$

$$dS = s_{in}\delta n_{in} - s_{out}\delta n_{out} + \frac{\delta Q}{T}$$

➡  $dU = (h_{in} - Ts_{in})\delta n_{in} - (h_{out} - Ts_{out})\delta n_{out} + TdS + \delta W_s + \delta W_\sigma$

Control volume with fixed boundary

$$dU = (h_{in} - Ts_{in})\delta n_{in} - (h_{out} - Ts_{out})\delta n_{out} + TdS + \delta W_s$$

Steady state or cycle:

$$\delta W_s = (h_{out} - Ts_{out})\delta n_{out} - (h_{in} - Ts_{in})\delta n_{in}$$

# Tank Evacuation by Isothermal Compressor

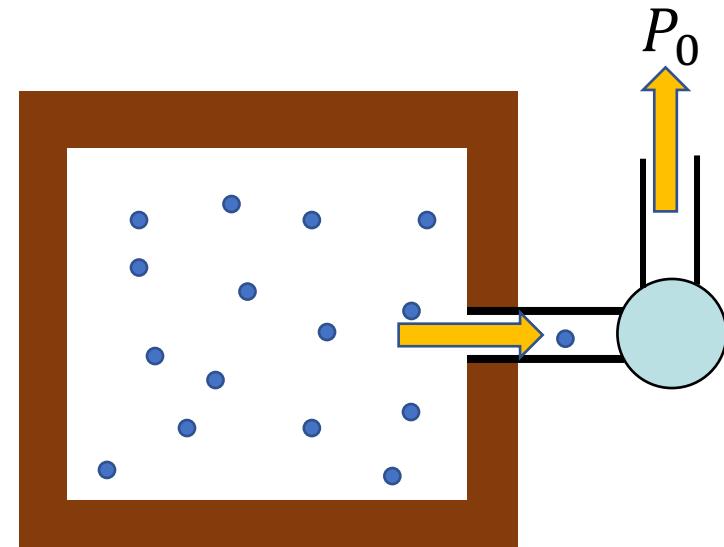
Initial:  $P_0$       Final:  $P$

Reversible work:

$$W_s = (P_0 - P)V - PV \ln \frac{P}{P_0}$$

Special case:  $P = 0$

$$W_s = P_0V$$



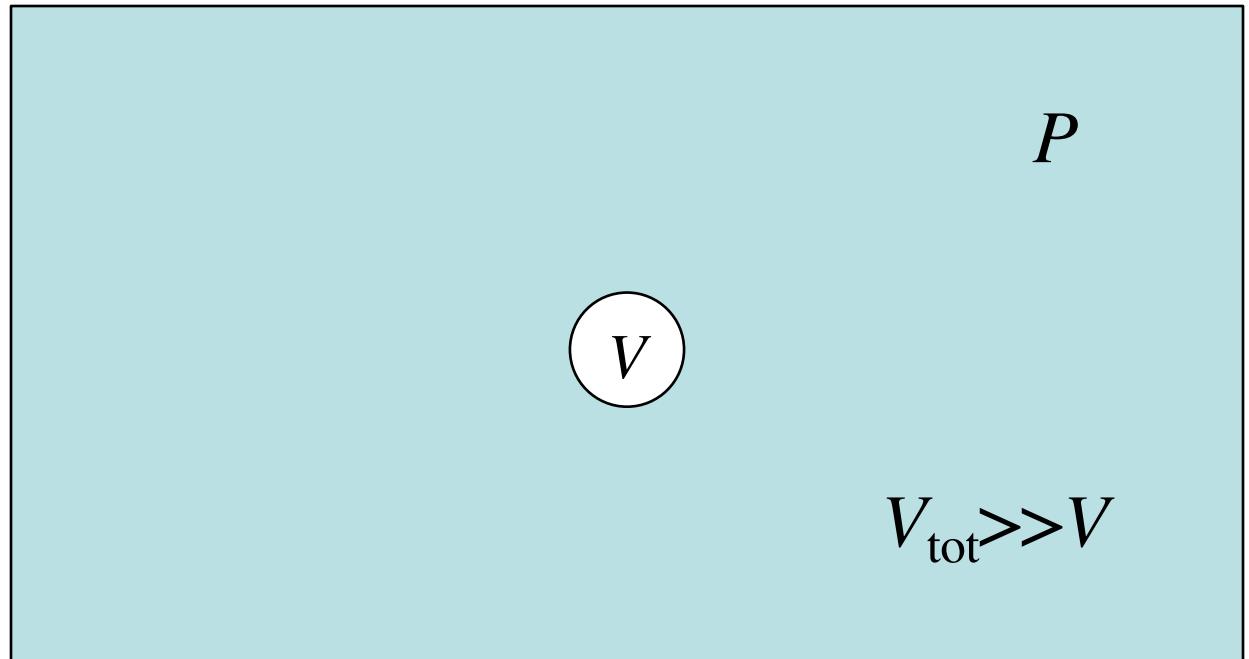
- Three routes:
- Tank + compressor as system
  - Compressor as system
  - Creating cavity of volume  $V$  in ambient pressure

Choose method based on mathematical convenience

# Cavity Work

The reversible work for creating a cavity of volume  $V$  in a large volume of fluid with pressure  $P$

$$W_s = PV$$



True for any fluids (gas or liquid, ideal or nonideal)

## Combined 1<sup>st</sup> and 2<sup>nd</sup> Law for Simple, Open System in Reversible Process

$$dU = h_{in}\delta n_{in} - h_{out}\delta n_{out} + \delta Q - pdV = hd\bar{n} + \delta Q - pdV$$

$$\delta Q = TdS - T(s_{in}\delta n_{in} - s_{out}\delta n_{out}) = TdS - Tsdn$$



$$dU = TdS - pdV + \mu dn$$

Generalize:

$$dU = TdS - pdV + \sum_i \mu_i dn_i$$

Fundamental eqn.

Subtle change in the meaning of differential

$$T = \left( \frac{\partial U}{\partial S} \right)_{v,\{n_i\}} \quad P = - \left( \frac{\partial U}{\partial V} \right)_{s,\{n_i\}} \quad \mu_i = \left( \frac{\partial U}{\partial n_i} \right)_{s,v,n_{j \neq i}}$$

## Questions to Think about

- Consider a box of ideal gas at equilibrium. Now imagine putting a thin partition wall that separated the box into two halves. Naively, there should be more configurations before the partition. Yes from thermodynamics we know the two states have the same entropy. Use the statistical expression for the entropy to show this is indeed the case, and explain the origin of this apparent paradox.
- Convince yourself of the result for the cavitation work for arbitrary fluids.