

# Thermodynamics: Phenomenology

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- Work and other forms of energy
  - Transfer and dissipation
- 1. & 2. Fundamental Laws of Thermodynamics
- Ideal-gas laws and simple processes
  - Technological applications, cyclic engines
- Real gases equation of state
  - Technological applications
- Phase equilibria
- Free energy in chemical reactions
  - Thermochemistry, electrochemistry
- Kinetic theory of gases

## Reading Assignments

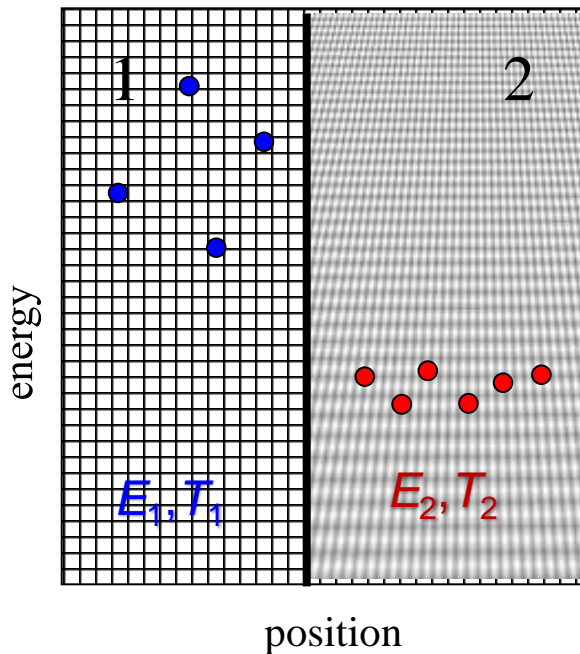
Weeks 11&12

LN V-VI:

Kondepudi Ch. 3 & 4  
Additional Material

McQuarrie & Simon  
Ch. 5 & 6

# 0. LTD: Systems in Thermal Contact Equilibrate



**Observation: (Zeroth Law TD)** systems in contact exchange energies until temperatures  $T_1 = T_2$

Disequilibrium: Two systems, 1 and 2, with fixed individual particle numbers and energies,  $T_1 \neq T_2$   
 $A_1 + A_2 = A$ ,  $E_1 + E_2 = E = \text{const.}$

# of states  $\Omega_1(E_1)$  and  $\Omega_2(E_2)$ , initially

**Isolated combined system**  $CS = 1+2$

→ total energy is fixed,  $E_1 + E_2 = E$ ,

but partition  $E_1/E_2$  can vary through heat ( $q$ ) exchange between 1 and 2 (no particle exchange).

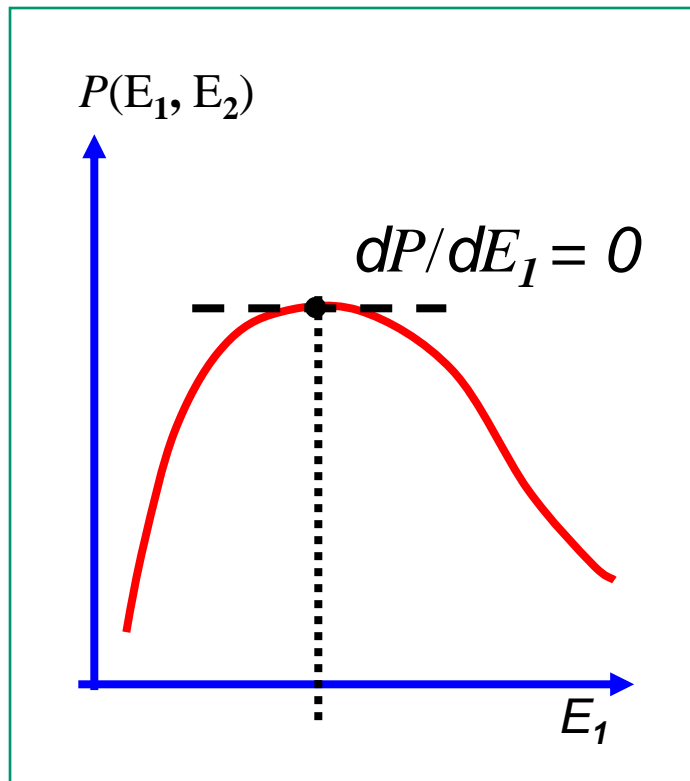
**Heuristic argument** (specific for exchange of  $q$  between systems,  $\approx$  postulate):

How likely is any  $E_1/E_2$ , how does it evolve in time?

Maximize  $P(E_1, E_2) \propto \Omega_{CS}(E_1, E_2) = \Omega_1(E_1) \cdot \Omega_2(E_2) = \Omega_1(E_1) \cdot \Omega_2(E - E_1)$

(We know: If all configurations are equally likely (Eta Theorem) → maximizes entropy)

# Maximizing Opportunities (# of states)



*Heuristic argument:* Maximize  $P(E_1, E_2)$

$$P(E_1, E_2) \propto \Omega_{\text{CS}}(E_1, E_2) = \Omega_1(E_1) \cdot \Omega_2(E - E_1)$$

Conservation of total energy  $E = E_1 + E_2 = \text{const}$

Heat energy ( $q$ ) transfer  $\rightarrow$  probability change,

constraint  $\Delta E_1 = -\Delta E_2 < 0$

*Product rule :*

$$\frac{dP}{dE_1} \propto \frac{d\Omega_1(E_1)}{dE_1} \Omega_2(E_2) + \Omega_1(E_1) \frac{d\Omega_2(E_2)}{dE_1}$$

$$= \frac{d\Omega_1(E_1)}{dE_1} \Omega_2(E_2) - \Omega_1(E_1) \frac{d\Omega_2(E_2)}{dE_2}$$

Maximum  $P$  :  $\frac{dP}{dE_1} = 0 \rightarrow \frac{1}{\Omega_1} \frac{d\Omega_1(E_1)}{dE_1} = \frac{1}{\Omega_2} \frac{d\Omega_2(E_2)}{dE_2} \neq 0$

# Entropy and Energy at Equilibrium

Many systems in mutual contact  $\rightarrow$  eventual stationary state – maximum probability  
all acquire *same temperature*  $T$

$$\left( \frac{1}{\Omega} \frac{d\Omega(E)}{dE} \right)_1 = \left( \frac{1}{\Omega} \frac{d\Omega(E)}{dE} \right)_2 = \left( \frac{1}{\Omega} \frac{d\Omega(E)}{dE} \right)_3 \dots \rightarrow \frac{d\Omega(E)}{\Omega dE} = \frac{d \ln[\Omega(E)]}{dE} = \text{const.}(E)$$

Independent of material, size, shape, amount (although limited variation at the time of experiments).  $\rightarrow$  Depends on energy, supplied to one of the systems as heat.  
Variable has dimension 1/energy.

But this heat energy dependent variable  $\text{const.}(E)$  is not extensive!

Suspect  $\text{const.} \sim$  temperature  $T =$  intensive variable depending on energy, since

System energy content of an ideal gas ( $N$  particles):  $P \cdot V = N \cdot k_B \cdot T$

Construct **intensive** energy variable:  $\langle E/N \rangle \sim \frac{P \cdot V}{N} = k_B \cdot T$

$$\frac{d \ln[\Omega(E)]}{dE} \propto \frac{d[S(\langle E \rangle)]}{d\langle E \rangle} = (\beta \cdot T)^{-1}$$

$$S(\langle E \rangle) \sim S_0 + \frac{\langle E \rangle}{T}$$

integration constant 

Simplest form  
compatible  
 $S$  extensive

# Conclusion: Entropy at Equilibrium

Define general thermodyn function  $S(E) = \text{constant} \cdot \text{Ln} \Omega(E) \geq 0$ ; for  $\Omega \geq 1$

$$S(E) = k_B \cdot \text{Ln} \Omega(E) \geq 0$$

$$\Omega(E) = e^{S(E)/k_B} \geq 1$$

System with  $\Omega = \#$  intrinsic states, initially in ground state  $T_{\text{sys}}, E \approx 0; S \approx 0$

brought in contact with "Heat Bath" at temperature  $T_{\text{hb}}$

spontaneously acquires heat energy  $\Delta \langle E \rangle = \Delta q \rightarrow$  stationary state

= **Thermal Equilibrium**: maximum spread of  $\Delta \langle E \rangle$  over  $\Omega$ , system  $\rightarrow T_{\text{sys}} \approx T_{\text{hb}}$

Then:  $S(E) = k_B \cdot \text{Ln} \Omega(E)$  (in appropriate units) and  $S(E) = S_{\text{max}}(E)$

$$S(\langle E \rangle) = \frac{\langle E \rangle}{T_{\text{sys}}} \geq 0$$

Heat absorption /  
emission by system @  $T_{\text{sys}}$

$$\Delta \langle E \rangle = \Delta q \rightarrow \Delta S = \frac{\Delta q}{T_{\text{sys}}}$$

sign  $\Delta S =$  sign  $\Delta q$

In spontaneous processes, entropy (always) increases:  $\Delta S > 0$

# Sample1: Path to Equilibrium

Energy dissipation by transfer of heat, dissipation, convection,...

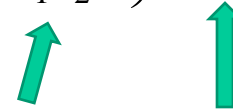
Entropy is a driving force for equilibration (Eta-Theorem)

*Irreversible entropy gains and losses*

$$\Delta S_1 = \frac{\Delta q_1}{T_1} = \frac{-\Delta q}{T_1} < 0 \quad \Delta S_2 = \frac{\Delta q_2}{T_2} = \frac{\Delta q}{T_2} > 0$$

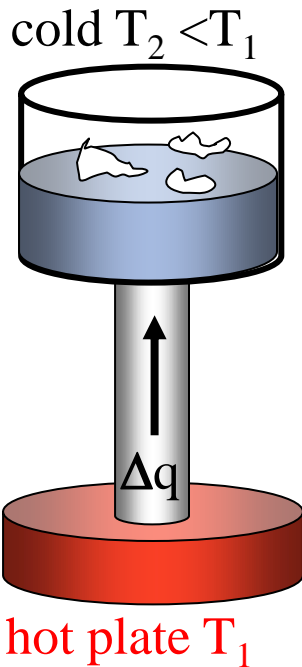
*Composite system :*

$$\Delta(S_1 + S_2) = \left( \frac{-1}{T_1} + \frac{1}{T_2} \right) \cdot \Delta q = \left( \frac{T_1 - T_2}{T_1 T_2} \right) \cdot \Delta q > 0$$



*General form  $dS_i = \text{driving Force} \cdot \text{irreversible flow}$*

Heat exchange as long as  $-\Delta S_1 = -\Delta q_1/T_1 < \Delta S_2 = \Delta q_2/T_2$



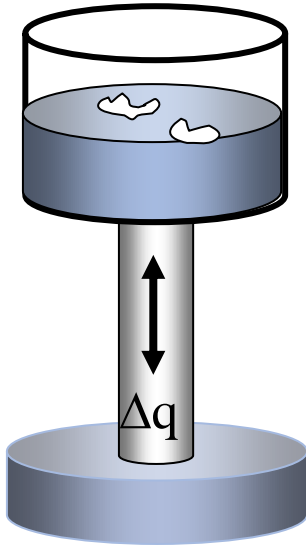
Note: In case of  $T_1 \approx T_2$ , heat can be exchanged isentropically, at  $S \approx \text{const.}$   
 Intrinsic energy distribution over  $\Omega$  is conserved  $\rightarrow$  reversible processes.

# Example1: Thermal Equilibrium

Energy dissipated evenly over entire system heat exchange ( $\Delta q$ ) back and forth, no net transfer,

$$\Delta q = \Delta U (= \Delta E). \quad \text{sign}(\Delta q) = \text{sign}(\Delta U)$$

warm  $T_2 = T$



warm plate:  $T_1 = T$

*Entropy gains and losses*

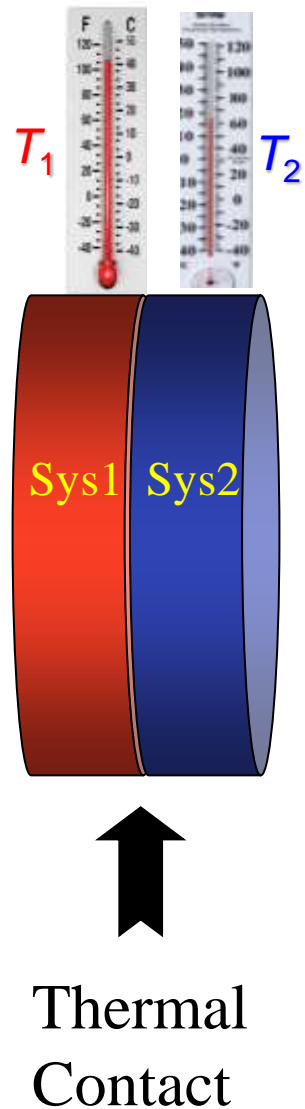
$$\frac{\Delta S_1}{\Delta U_1} = \frac{\Delta S_1}{\Delta q_1} = -\frac{\Delta S_1}{\Delta q} = \frac{1}{T}$$

$$\frac{\Delta S_2}{\Delta U_2} = \frac{\Delta S_2}{\Delta q_2} = +\frac{\Delta S_2}{\Delta q} = \frac{1}{T}$$

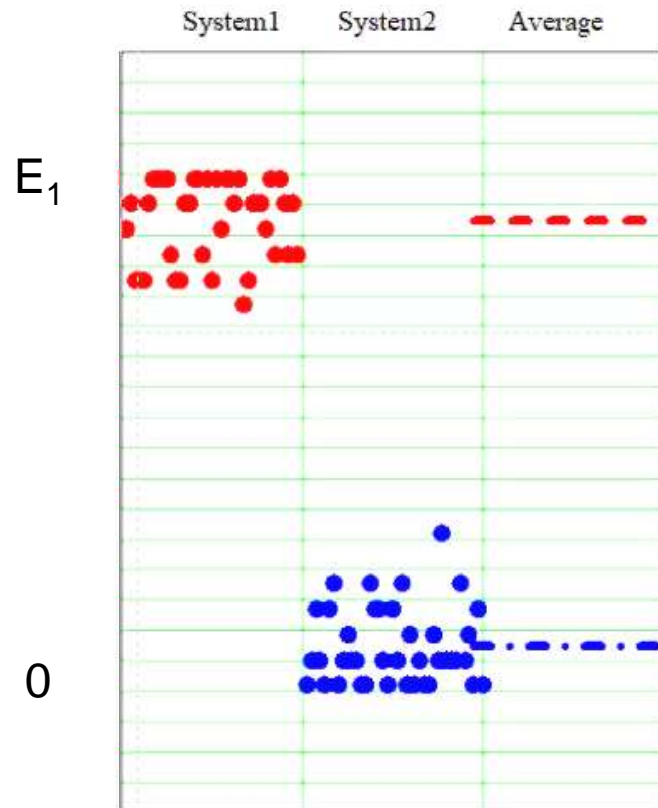
For any system at temperature  $T_{low}$  in contact with others at  $T_{high} > T_{low}$  :  
Equilibration occurs with heat absorption at  $T_{low}$  : entropy gain

**$\Delta S = \Delta q / T_{low}$**  regardless of substance and construction!

# Simulation: Energy Equilibration



Observation:  $t$ -dependent equilibration of temperatures



Discrete energy states of **interacting systems**

Initial conditions

$$\langle E_1 \rangle \approx E \quad \langle E_2 \rangle \approx 0$$

Random  $\pm$  energy and  $\pm$  momentum exchange

Initial mean energies

$$e_1 = E_1/A_1 \neq e_2 = E_2/A_2$$

Final mean energies

*thermalization*  $e_i \rightarrow T_i = T$

*energy fluctuations*

$$\sigma_{e_i}^2 = k_B T^2 C_V$$



## 2. Law RD: Entropy of Ideal Gases

Entropy  $S$  of a system  $\leftrightarrow$  distribution of entire energy content over all  $\Omega$  accessible states

$\rightarrow$  closed (isolated) systems in equilibrium  $S = S_{\max} = \text{const.}$

for e.g., system + entire surrounding

In *internal disequilibrium*:  $dS = dS_{\text{intr}} > 0 \rightarrow$  spontaneous, irrev. process  
disparity in temperature  $\rightarrow$  thermal driving force  $F$ , drives irreversible  
heat flow  $dq \rightarrow dS = F \cdot dq$  (heat flow carries entropy)

Mass or energy exchange  $\rightarrow dS_{\text{exch}} \geq \frac{q}{T}$  system temperature  $T$

Iso-thermalization ( $T$ -equilibration) of systems in thermal contact through redistribution of heat energy,  $q =$  randomized energy  $\rightarrow dU = T \cdot dS$ .

Generally:  $dU = T \cdot dS + w = T \cdot dS - P \cdot dV$

## 2. Law RD: Entropy of Ideal Gases

Iso-thermalization ( $T$ -equilibration) of systems in thermal contact through redistribution of heat energy,  $q$  = randomized energy  $\rightarrow dU = T \cdot dS$ .

Generally:  $dU = T \cdot dS + w = T \cdot dS - P \cdot dV$

$$T \cdot dS = \left( \frac{\partial U}{\partial V} \right)_T dV + \left( \frac{\partial U}{\partial T} \right)_V dT + P \cdot dV$$

Ideal gas :  $U = N(3/2)k_B T = \text{only a function}(T) \rightarrow \left( \frac{\partial U}{\partial V} \right)_T = 0$

Ideal gas  $\rightarrow dS = \left( \frac{\partial U}{\partial T} \right)_V \frac{dT}{T} + \frac{P}{T} \cdot dV \rightarrow dS = \left( \frac{\partial U}{\partial T} \right)_V \frac{dT}{T} + Nk_B T \cdot \frac{dV}{V}$  *integrate DEq*

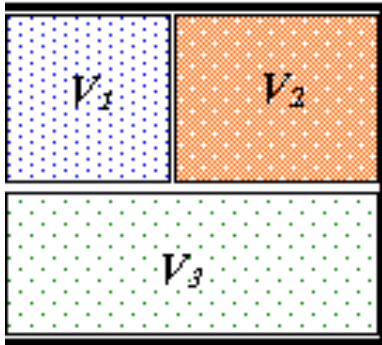
**Ideal Gas  
@ equilibrium**

$$S(V, T, N) = \underbrace{S_0(V_0, T_0, N)}_{\text{Integration constant, initial state}} + N \cdot C_V \cdot \ln\left(\frac{T}{T_0}\right) + N \cdot R \cdot \ln\left(\frac{V}{V_0}\right)$$

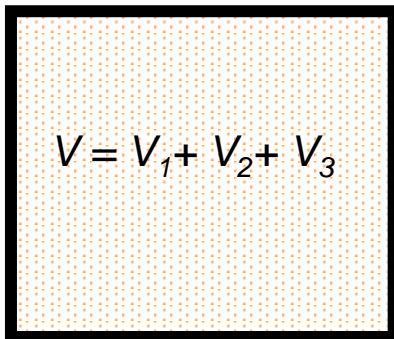
Integration constant, initial state

## Example 2: Entropy of Mixing

Separated Gases



Mixed Gases



Dilute (ideal) gas type in separated  $V_i$ ;  $i = 1, 2, 3$ ;  
all at same  $P$ ,  $T$ . **No external energy transfer.**

Remove divisions  $\rightarrow$  **spontaneous mixing** occurs

$\rightarrow$  less ordered, more randomized energy  $\rightarrow S \nearrow ?$

*Entropy change due to mixing :*

$$\Delta S = S_{mix} - S_{unm} = R \cdot [Ln \Omega_{mix} - Ln \Omega_{unm}] = R \cdot Ln \left[ \frac{\Omega_{mix}}{\Omega_{unm}} \right]$$

*Plausible assumption* : #states  $\Omega_i \propto V_i$   $i = 1, 2, 3$

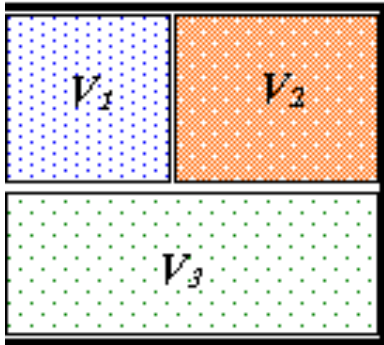
*Gain by individual components*

$$\Delta S_i = n_i \cdot R \cdot \ln \left( \frac{V}{V_i} \right) > 0 \quad n_i = \text{number of moles } i$$

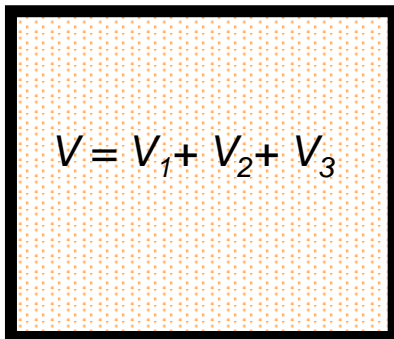
Quantum Mechanics (particle-in-box, phase space): Smaller volumes  $\rightarrow$  fewer states

# EoS: Entropy of Mixing

Separated Gases



Mixed Gases



S - gain by individual gas components

$$\Delta S_i = n_i \cdot R \cdot \ln\left(\frac{V}{V_i}\right) > 0 \quad n_i = \text{number of moles } i$$

*Entropy is extensive (additive).* → components add

$$\rightarrow \Delta S = -R \cdot \sum_i n_i \cdot \ln\left(\frac{V_i}{V}\right) > 0 \quad S \nearrow$$

total moles  $n = \sum_i n_i \rightarrow \Delta S = -n \cdot R \cdot \sum_i \left(\frac{n_i}{n}\right) \cdot \ln\left(\frac{V_i}{V}\right)$

*Relative abundance (probability for) particle type i*

$$p_i = \frac{n_i}{n} = \frac{V_i}{V} < 1$$

$$\Delta S = -n \cdot R \cdot \sum_i p_i \cdot \ln p_i \quad n \text{ moles}$$

$$N \text{ particles} \quad \Delta S = -N \cdot k_B \cdot \sum_i p_i \cdot \ln p_i$$

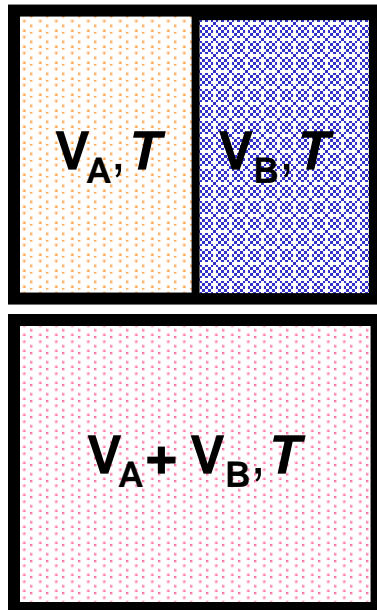
Can use other "State Functions" to calculate entropy, all related by EoS

# Entropy of Mixing: Example

One mole each of two gases, **A** and **B**, in the respective halves of a separated container at  $P_A = P_B = 1 \text{ atm}$ ,  $T_A = T_B = 298 \text{ K}$

When the partition is removed, the gases will mix. **No change in energy**

Calculate the entropy gain or loss in the mixing of the two gases.



Total  $n = 2 \text{ moles}$ ; Mole fractions:  $n_A/n = n_B/n = 0.5$ .

Abundances, probabilities are  $p_A = p_B = 0.5$

The entropy of mixing is given by

$$\begin{aligned}\Delta S_{mix} &= -nR \left\{ \frac{n_A}{n} \cdot \text{Ln} \left( \frac{n_A}{n} \right) + \frac{n_B}{n} \cdot \text{Ln} \left( \frac{n_B}{n} \right) \right\} = \\ &= -2R \{ 0.5 \cdot \text{Ln}(0.5) + 0.5 \cdot \text{Ln}(0.5) \} = 11.5 \frac{\text{J}}{\text{K}} > 0\end{aligned}$$

Entropy is gained  $\leftrightarrow$  mixing occurs spontaneously.

**Mixing cannot be simply reversed  $\rightarrow$  Maxwell's Demon does not exist!**

# A Good Question

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**Q:** The mixing of two gases at  $p = 1 \text{ atm}$  and  $T = 298 \text{ K}$  yields an entropy gain of  $\Delta S_{\text{mix}} = 11.5 \text{ kJ/K}$ . How much heat will be generated, emitted or absorbed?

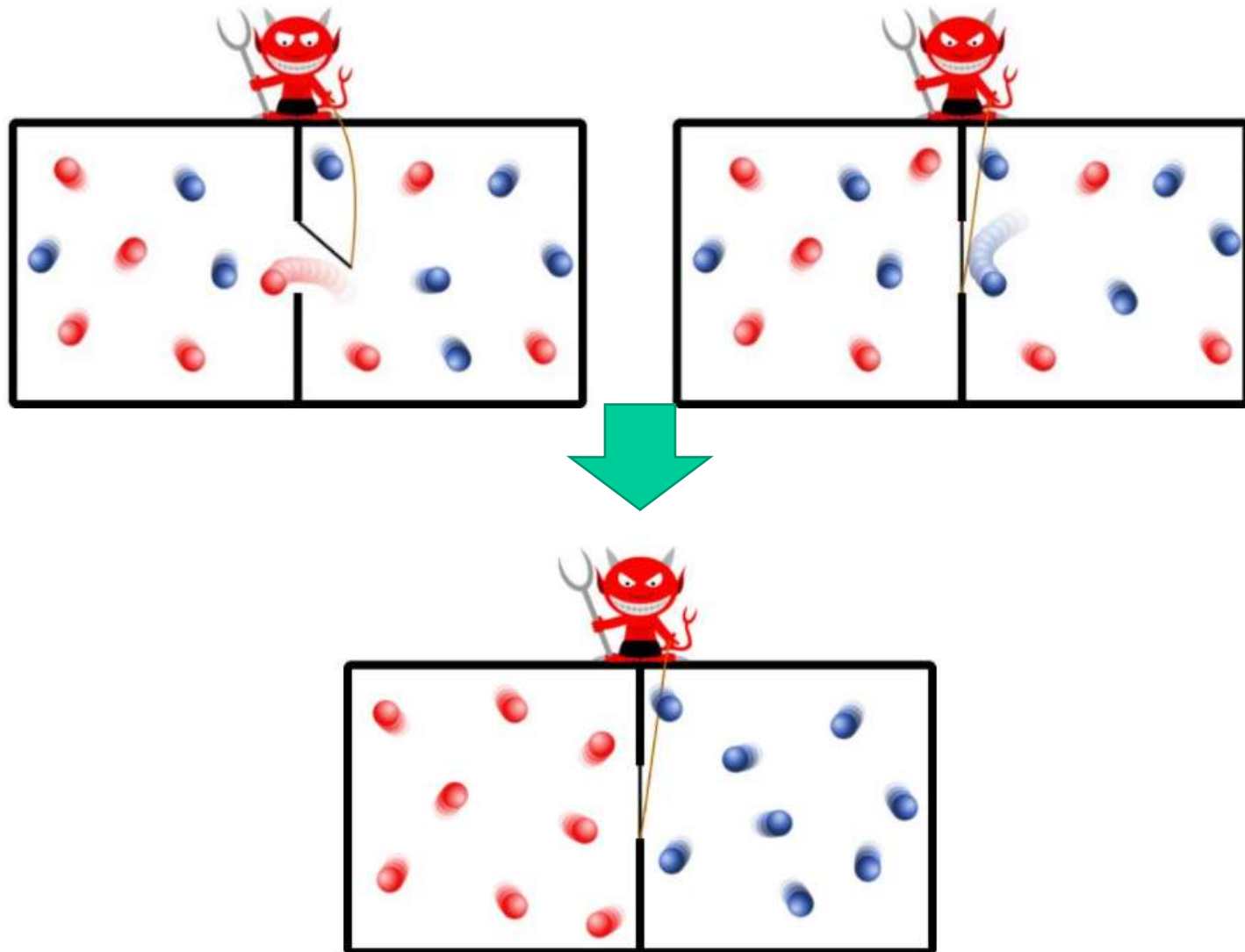
**A:** None. Because all gases are at same temperature, the mixing does not change energy. The mixing process is spontaneous and irreversible. An entropy gain of  $\Delta S_{\text{mix}} = +11.5 \text{ kJ/K}$  at  $T = 298 \text{ K}$  only means that  $q_{\text{irrev}} < T \cdot \Delta S_{\text{mix}}$ . Absence of heat,  $q_{\text{irrev}} = 0$ , is compatible with the Second Law TD.

**Mixing cannot be simply reversed → Maxwell's Demon does not exist!**

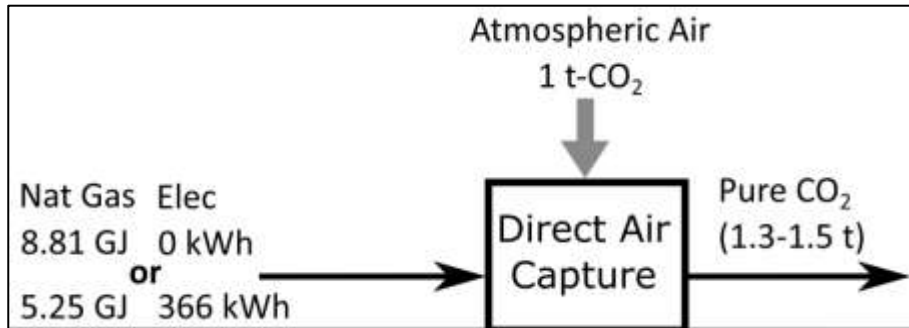
# De-Mixing by Maxwell's Demon

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# Carbon Capture and Sequestration



Unmixing CO<sub>2</sub> from directly captured atmospheric gas supply.

→ → \$94-\$232 per ton CO<sub>2</sub>.

When CO<sub>2</sub> is delivered at 15

MPa, theoretical design requires either 8.81 GJ of natural gas, or 5.25 GJ of gas plus 366 kWh of electricity, per ton of CO<sub>2</sub> captured.

→ Levelized cost per t-CO<sub>2</sub> from atmosphere ranges from \$94 to \$232/t-CO<sub>2</sub>.<sup>A</sup>

Keith et al., A Process for Capturing CO<sub>2</sub> from the Atmosphere, Joule (2018),  
<https://doi.org/10.1016/j.joule.2018.05.006>



## Conclusion: 2<sup>nd</sup> Law of Thermodynamics

Define general thermodyn function  $S(E) = \text{constant} \cdot \text{Ln} \Omega(E) \geq 0$ ; for  $\Omega \geq 1$

$$S(E) = k_B \cdot \text{Ln} \Omega(E) \geq 0$$

$$\Omega(E) = e^{S(E)/k_B} \geq 1$$

**Equilibrated Systems Have Maximum Entropy.**

**Spontaneous Transitions Always Increase System Entropy.**

$$S(V, T, N) = S_0(V_0, T_0, N) + N \cdot C_v \cdot \text{Ln} \left( \frac{T}{T_0} \right) + N \cdot R \cdot \text{Ln} \left( \frac{V}{V_0} \right)$$

Randomized internal energy :  $\langle E \rangle = T \cdot S$

Processes with heat transfer  $\Delta q$  @  $T \approx \text{const}$  can be reversed

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# Three Modes of Energy Transfer

