Consider work performed by a system in an isothermal expansion:

\[ P_1 = 15 \text{ atm} \quad V_1 = 1 \text{ L} \]

\[ P_2 = 1 \text{ atm} \quad V_2 = 15 \text{ L} \]

If the pins are removed what happens?

What is the change in internal energy?

\[ \Delta U = U_1 - U_2 \propto \Delta T \quad \therefore \quad \Delta U = 0 \]

What is the change in enthalpy?

\[ \Delta H = H_1 - H_2 = (U_2 + P_2 V_2) - (U_1 + P_1 V_1) \]

\[ \Delta H = 0 \]

Note: this does not mean that \( q \) or \( w \) is 0, only that \( q=-w \). In fact \( w = -P_{ex}\Delta V \).

\[ 1 \text{ atm} = 101.325 \text{ kPa} \]

\[ w = -101.325 \text{ kPa (14 L) (10}^{-3} \text{ m/L)} \]

\[ w = -1.42 \text{ kJ} \quad q = 1.42 \text{ kJ} \]
The work performed in an isothermal expansion is pathway dependent:

\[ w = - P_2 \Delta V = -1.42 \text{ kJ} \]

\[ w = - \int_{V_1}^{V_2} P \, dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V} \]

\[ w = -nRT \ln \left( \frac{V_2}{V_1} \right) = -4.12 \text{ kJ} \]

\[ w = -(101.325 \text{ kPa/atm}) \times (15 \text{ L}) \times (10^{-3} \text{ m/L}) \times \ln(15) \]

A *reversible* process is in equilibrium at each step.
Consider:

Calculate $\Delta H$ in kJ/mol

\[
\begin{align*}
\text{NaCl}_\text{(s)} & \rightarrow \text{Na}^+\text{(aq)} + \text{Cl}^-\text{(aq)} \\
\Delta H &= -167.16 - 240.12 - (-411.15) = 3.87 \text{ kJ/mol}
\end{align*}
\]

This is an endothermic reaction - but clearly spontaneous, as was the endothermic reaction demonstrated in class.

\[
2\text{NH}_4\text{SCN}_\text{(s)} + \text{Ba(OH)}_2\cdot8\text{H}_2\text{O}_\text{(s)} \rightarrow 2\text{NH}_3\text{(g)} + \text{Ba(SCN)}_2\text{(s)} + 10\ \text{H}_2\text{O}_\text{(l)}
\]

The reverse reactions are not spontaneous.

Qualitatively: “Nature Prefers Disorder”

\[
\begin{align*}
\text{NaCl}_\text{(s)} \text{ “Ordered”} & \rightarrow \text{Na}^+\text{(aq)} + \text{Cl}^-\text{(aq)} \text{ “Disordered”}
\end{align*}
\]
Entropy is the quantitative thermodynamic measure of disorder.

Consider a system with 3 balls

A state of the system is 1 ball in each bowl.

Another state is 2 balls in bowl 1, 1 ball in bowl 2.

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Two gas bulbs of equal size

Gas Molecules

The probability of any one molecule being in A is \( W = \frac{1}{2} \)

Any two molecules in A is \( W = \frac{1}{2} \cdot \frac{1}{2} = \frac{1}{4} \)

Any three molecules in A is \( W = \frac{1}{2} \cdot \frac{1}{2} \cdot \frac{1}{2} = \frac{1}{8} \)

Probability of N molecules in A

\[ W = \left( \frac{1}{2} \right)^N \]

Coin Flips

\[ \left( \frac{1}{2} \right)^1 \]

\[ \left( \frac{1}{2} \right)^2 \]

\[ \left( \frac{1}{2} \right)^3 \]

N consecutive heads

\[ W = \left( \frac{1}{2} \right)^N \]
Entropy is the quantitative thermodynamic measure of disorder.

Consider a system with 3 balls and 3 bowls:

A state of the system is 1 ball in each bowl.

- **6 Possibilities**
  
  \[
  \# = \frac{N!}{N_1!N_2!N_3!}
  \]

  - 6 Possible arrangements:
    - ABC
    - ACB
    - BAC
    - BCA
    - CAB
    - CBA

  \[
  W = \frac{6}{18} = \frac{1}{3}
  \]

Another state is 2 balls in bowl 1, 1 ball in bowl 2.

- **3 Possibilities**
  
  \[
  \# = \frac{3!}{1!1!1!}
  \]

  - 3 Possible arrangements:
    - AB
    - AC
    - BC

  \[
  W = \frac{3}{18} = \frac{1}{6}
  \]

Or 3 balls in bowl 1.

- **1 Possibility**
  
  \[
  \# = \frac{3!}{3!0!0!}
  \]

  - Only one arrangement possible:
    - ABC

  \[
  W = \frac{1}{18}
  \]
**Statistical definition of entropy (S) for a state:**

\[ S = k \ln W \]

- **W** \( \propto \) probability of a state, degeneracy of a state, and/or number of microstates
- **k** = Boltzmann Constant
  \[ 1.3805 \times 10^{-23} \text{ J K}^{-1} \]
- \( \therefore \) **S** has units of J K\(^{-1}\)

**S is an extensive function.**

\[ W = \left( \frac{1}{2} \right)^5 = \frac{1}{32} \]

\[ S = -3.47 \text{ k} \]

\[ W = \left( \frac{1}{2} \right)^{10} = \frac{1}{1024} \]

\[ S = -6.93 \text{ k} \]

**S is a state function.**

The value of **S** depends on the state, not on how the state was reached.
Thermodynamic definition of entropy ($S$):

$$dS = \frac{dq_{rev}}{T}$$

Heat that would be transferred in a reversible process

$$\Delta S = S_B - S_A = \int_A^B \frac{dq_{rev}}{T}$$

Adding heat increases the entropy of the system.

The entropy of the system increases in an isothermal expansion.
Entropy change in a system is calculated from reversible heat:

Reversible expansion

\[ w = - P_2 \Delta V = -1.42 \text{ kJ} \]

Irreversible expansion

\[ q = -w = 1.42 \text{ kJ} \]

\[ w = - nRT \ln \left( \frac{V_2}{V_1} \right) = -4.12 \text{ kJ} \]

\[ q_{\text{rev}} = -w_{\text{rev}} = 4.12 \text{ kJ} \]

\[ \Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T} = \frac{4.12 \text{ kJ}}{298 \text{ K}} = 13.8 \text{ J K}^{-1} \]
Consider the isothermal expansion of an ideal gas.

Thermodynamic definition:

\[
\Delta S = S_B - S_A = \int_{A}^{B} dq_{\text{rev}} \quad = \int_{A}^{B} \frac{dq_{\text{rev}}}{T} = \frac{1}{T} \int_{A}^{B} dq_{\text{rev}} = \frac{q_{\text{rev}}}{T}
\]

isothermal \(\Rightarrow\) \(\Delta U = q + w = 0 \quad w_{\text{rev}} = -nRT \ln \left(\frac{V_2}{V_1}\right) \quad q_{\text{rev}} = nRT \ln \left(\frac{V_2}{V_1}\right)\)

\[
\Delta S = nR \ln \left(\frac{V_2}{V_1}\right)
\]

entropy change in the isothermal expansion of an ideal gas.

Statistical definition (counting states): \(S = k \ln W\)

\[
\Delta S = k \ln \left(\frac{V_2}{V_1}\right)^N - k \ln \left(\frac{V_1}{V_1}\right)^N
\]

\[
\Delta S = k \ln \left(\frac{V_2}{V_1}\right)^N = N k \ln \left(\frac{V_2}{V_1}\right)
\]

\[
\Delta S = \frac{N}{N_A} N_A k \ln \left(\frac{V_2}{V_1}\right) = nR \ln \left(\frac{V_2}{V_1}\right)
\]

\[
\Delta S = nR \ln \left(\frac{V_2}{V_1}\right)
\]