

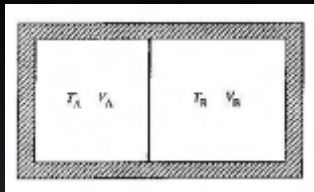
# More on entropy

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# $dS > 0$ for irreversible process in isolated sys.



Composite system made of two subsystems (A and B) at different temperatures  $T_A$  and  $T_B$ . No heat exchange and doing no work  $\Rightarrow$  Isolated system

$$U = U_A + U_B \Rightarrow dU_A = -dU_B \text{ and } S = S_A + S_B \Rightarrow dS = dS_A + dS_B$$

$$dS_A = \frac{dU_A}{T_A} \quad \text{Why?}$$

$$dS = \frac{dU_A}{T_A} + \frac{dU_B}{T_B} \quad \Rightarrow dS = dU_A \left( \frac{1}{T_A} - \frac{1}{T_B} \right)$$

$dS$  is always positive. **Hope you can show this!**

## The quantity $q_{\text{rev}} - q$ is positive

Conduct a change of state by two paths: one reversible and another irreversible

$$dU = Dq + Dw \quad dU = Dq_{\text{rev}} + Dw_{\text{rev}}$$

The change in internal energy for the two paths is the same, so

$$Dq_{\text{rev}} - Dq = Dw - Dw_{\text{rev}}$$

The right hand side of this equation is always positive (**Don't forget the sign of  $w$** )

## Clausius inequality says that $dS \geq \frac{Dq}{T}$

A system undergoing irreversible heat exchange  $Dq$

$$dS = \frac{Dq_{\text{rev}}}{T} = \frac{Dq}{T} + \frac{Dq_{\text{rev}} - Dq}{T}$$

The second term shown to be always positive. Hence,

$$dS \geq \frac{Dq}{T}$$

Alternatively,

$$dS = dS_{\text{exch}} + dS_{\text{irr}},$$

where

$$dS_{\text{exch}} = \frac{Dq}{T} \text{ and } dS_{\text{irr}} = \frac{Dq_{\text{rev}} - Dq}{T}$$

First term may be positive or negative depending on the sign of  $q$  but the second is always positive

# Entropy change of an ideal gas

Isothermal, reversible

$$Dq_{\text{rev}} = -Dw_{\text{rev}} = \frac{RT}{V}$$

$$dS = Dq_{\text{rev}}/T = R/V$$

$$\Delta S = R \ln \frac{V_2}{V_1}$$

Adiabatic, reversible

$$Dq_{\text{rev}} = 0$$

$$\Delta S = 0$$

# Equilibrium phase transition $\Delta S = \frac{\Delta H}{T}$

Consider the transformation  $\text{H}_2\text{O}(\text{l}, 0\text{ }^\circ\text{C}) \longrightarrow \text{H}_2\text{O}(\text{s}, 0\text{ }^\circ\text{C})$  at atmospheric pressure

Equilibrium transformation at constant  $T$  and  $P$

$$q_P = \Delta H$$

$$\Delta S = \frac{\Delta H}{T}$$

Caution: Express  $T$  in K

# Reversible path for irreversible processes

Consider expansion of an ideal gas into vacuum with no heat transfer

$$Dq = 0 \text{ and } Dw = 0 \Rightarrow dU = 0$$

No temperature change on free expansion of an ideal gas (why?)  
Construct a reversible path between the initial and final state -  
isothermal, reversible

$$\Delta S = R \ln \frac{V_2}{V_1}$$

Note:  $\Delta S > 0$  as the process is irreversible and the system is isolated

# Entropy change during a temperature change

Consider the transformation  $\text{H}_2\text{O}(l, 0\text{ }^\circ\text{C}) \rightarrow \text{H}_2\text{O}(l, 100\text{ }^\circ\text{C})$  at atmospheric pressure

Heating at constant  $P$  (reversible or irreversible)

$$Dq_{\text{rev},P} = dH = C_P dT$$

$$dS = \frac{Dq_{\text{rev},P}}{T} = \frac{C_P dT}{T}$$

$$\Delta S = C_P \ln \frac{T_2}{T_1}$$

Caution:  $T$  in K



# Entropy for $\text{H}_2\text{O}(\text{l}, -10^\circ\text{C}) \rightarrow \text{H}_2\text{O}(\text{s}, -10^\circ\text{C})$

- 1 Heat liquid water from  $-10^\circ\text{C}$  to  $0^\circ\text{C}$

$$\Delta S_1 = C_P(\text{liq}) \ln \frac{273}{263}$$

- 2 Equilibrium phase transformation at  $0^\circ\text{C}$

$$\Delta S_2 = \frac{\Delta_{\text{freezing}}H}{273}$$

- 3 Cool ice from  $0^\circ\text{C}$  to  $-10^\circ\text{C}$

$$\Delta S_1 = C_P(\text{ice}) \ln \frac{263}{273}$$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$\Delta S_{\text{surr}} = -\Delta H_{\text{sys}}/263 = -\Delta_{\text{freezing}}H(263\text{K})/263$$