Lecture 9

Thursday, October 3, 2024 09:59

The Clausius Inequality

$$|dw_{rev}| \geq |dw|$$

negative negative

$$-dw_{rev} \geq -dw$$

$$dw - dw_{rev} \geq 0$$

$$dU = dw + dq = dw_{rev} + dq_{rev}$$

$$dw - dw_{rev} = dq_{rev} - dq$$

$$dq_{rev} - dq \geq 0$$

$$dq_{rev} \geq dq$$

divide by T

$$\frac{dq_{rev}}{} \geq \frac{dq}{}$$

$$T \qquad \geq \qquad T$$

$$\boxed{dS \geq \frac{dq}{T}}$$ Clausius Inequality

For an isolated system, $dq = 0$, so

$$dS \geq 0$$

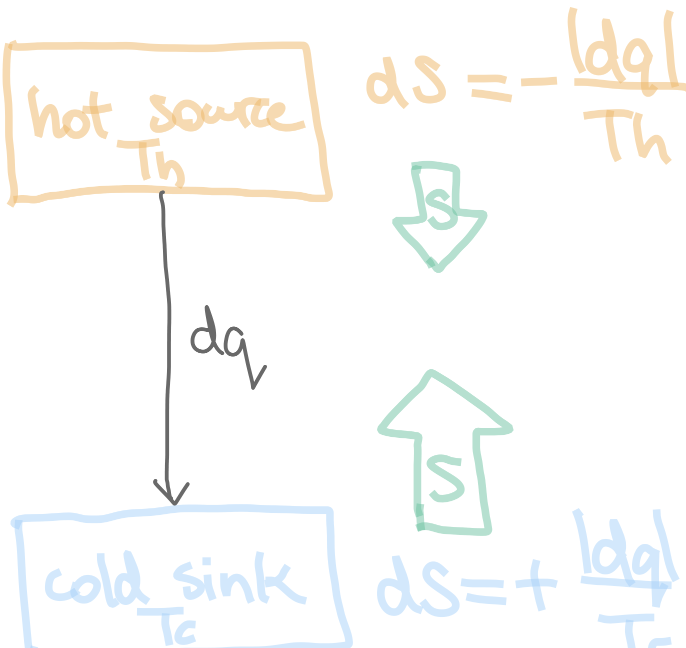
The entropy cannot decrease in an isolated system spontaneously.

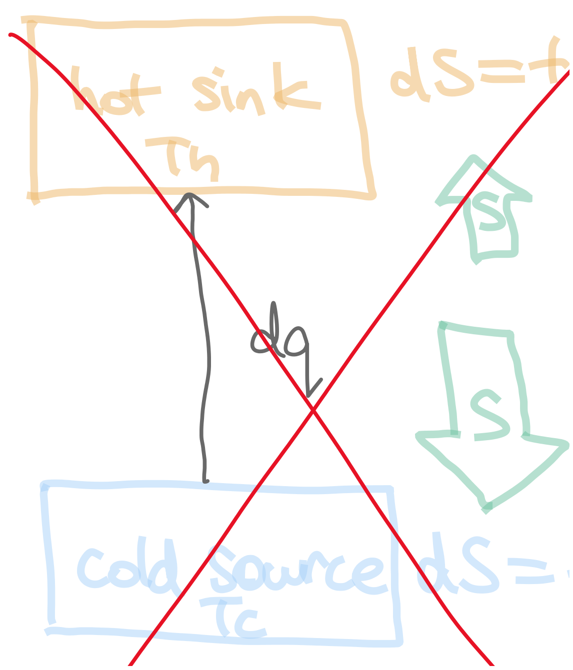
$$dS_{tot} = dS + dS_{sur} \geq 0$$

irreversible ($>$)

reversible ($=$)

$$dS_{tot} = 0 \quad \text{equilibrium}$$





$\Delta S_{tot} > 0$ ~~$\Delta S_{tot} < 0$~~

Topic 3B: Entropy Changes for Specific Processes

Previously, discussed ΔS for expans

$$\Delta S = nR \ln \frac{V_f}{V_i}$$ isothermal, perfect gas

Case 1: Reversible Expansion

$$dq_{sur} = -dq$$

$$dq_{rev} = nRT \ln\left(\frac{V_f}{V_i}\right)$$

$$dq_{sur} = -nRT \ln\left(\frac{V_f}{V_i}\right)$$

$$\Delta S_{sur} = -\frac{q_{rev}}{T} = -nR \ln \frac{V_f}{V_i}$$

$$\boxed{\Delta S_{tot} = 0}$$

Case 2: Free Expansion

$w = 0$

isothermal, $\Delta U = 0 = C_v \Delta T$

$\Delta U = q + w$, $q = 0$

$\Delta S_{sur} = 0$

but $\Delta S = nR \ln \frac{V_f}{V_i}$

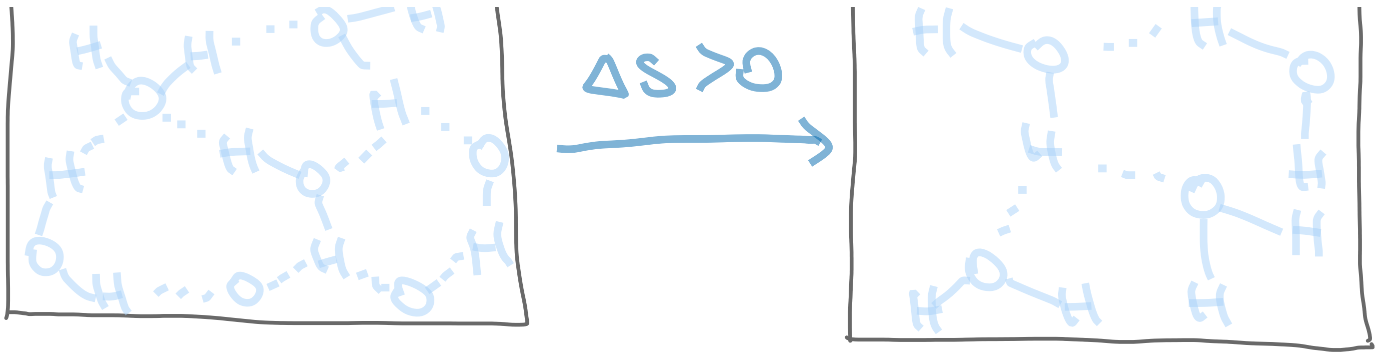
$$\boxed{\Delta S_{tot} = \Delta S + \Delta S_{sur} = nR \ln \frac{V_f}{V_i}}$$

Phase Transitions

T_{trs}, normal transition temperature

the temperature at which two

phases are in equilibrium at 1 a



solid H_2O
regular H-bond network

liquid H_2O
H-bonding still present, but no crystallinity

$$\boxed{\Delta_{trs} S = \frac{\Delta_{trs} H}{T_{trs}}}$$

$\Delta_{trs} S^\ominus$ for a few compounds

	at T_f (fusion)	at T_b
Ar	14.17	74.53
H_2O	22.00	109.0
C_6H_6	38.00	87.19

<u>Heating</u>

T_f

darev

$$S(T_f) = S(T_i) + \int_{T_i} \frac{\cdots}{T}$$

$$S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{C_p dT}{T}$$

$dH = C_p dT$, $dq_{rev} = dH$ at constant pressure

Assume C_p constant in T_i to T_f,

$$S(T_f) = S(T_i) + C_p \int_{T_i}^{T_f} \frac{1}{T} dT$$

$$\boxed{S(T_f) = S(T_i) + C_p \ln \frac{T_f}{T_i}}$$

$$\int \frac{1}{x} dx = \ln |x|$$

<u>Composite Processes</u>

Consider different steps in a path

that we can calculate to obtain the final result.

Practice Problem

Calculate the entropy change when argon at 25°C and 1.00 bar is allowed to expand to 1.000 dm^3 and simultaneously heated to 100°C. Use $C_{V,m} = \frac{3}{2}R$. $V_i = 0.500\ dm^3$

Solution: first, find n

$$p_i V_i = nRT$$

$$n = \frac{p_i V_i}{RT}$$

$$n = \frac{100{,}000\ Pa \cdot 0.500 \times 10^{-3}\ m^3}{8.3145\ J \cdot K^{-1} \cdot mol^{-1} \cdot 298\ K}$$

$$n = 0.0201\ mol$$

Isothermal expansion:

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

$$= 0.0201\,mol \cdot 8.3145\,J \cdot K^{-1} \cdot$$

$$\cdot \ln \frac{1.000\,dm^3}{0.500\,dm^3}$$

$$\Delta S(1) = +0.116\,J \cdot K^{-1}$$

Heating:

$$\Delta S(2) = n C_{V,m} \ln \frac{T_f}{T_i}$$

$$= \frac{3}{2} \cdot 0.0201\,mol \cdot 8.3145\,J \cdot$$

$$\cdot \ln \frac{373\,K}{298\,K}$$

$$= +0.0564\,J \cdot K^{-1}$$

$$\Delta S = \Delta S(1) + \Delta S(2)$$

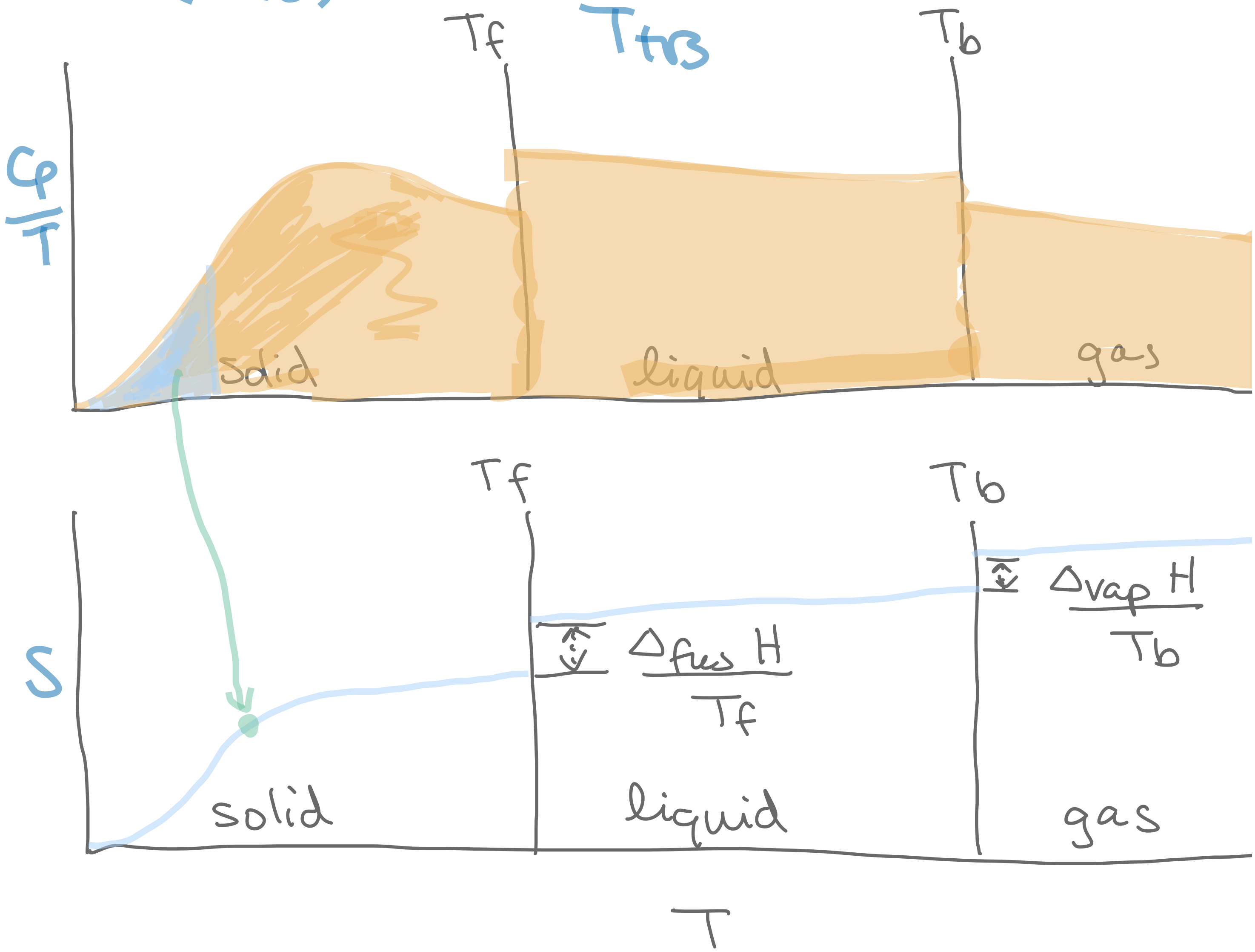
$$= (0.116 + 0.0564)\,J \cdot K^{-1}$$

$$\boxed{\Delta S = +0.173\ \mathrm{J \cdot K^{-1}}}$$

Topic 3C: The Measurement of Entro

$$S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{C_p(T)}{T}\, dT$$

$$\Delta S(T_{trs}) = \frac{\Delta_{trs}H(T_{trs})}{T_{trs}}$$



$$S_m(T) = S_m(0) + \int_0^{T_f} \frac{C_{p,m}(s,T')}{T'}\, dT'$$

$$+ \frac{\Delta_{fus} H}{T_f} + \int_{T_f}^{T_b} \frac{C_{p,m}(l,T')}{T'}$$

$$+ \frac{\Delta_{vap} H}{T_b} + \int_{T_b}^{T} \frac{C_{p,m}(g,T')}{T'}\, dT'$$