

At the limit of short steps if and cd

$$\frac{\delta Q_{if}}{T_{if}} + \frac{\delta Q_{co}}{T_{cd}} \Rightarrow \oint \left(\frac{\delta Q}{T} \right)_{rev} = 0$$

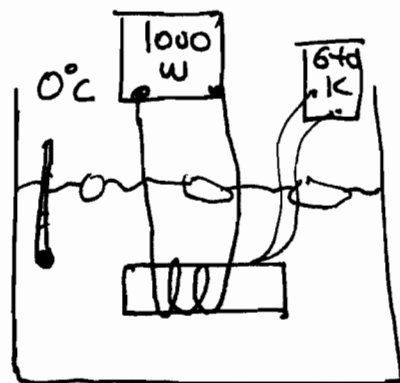
This allows us to define a new state function, the entropy \underline{S} :

$$\Delta \underline{S} = \int_A^B \left(\frac{\delta Q}{T} \right)_{rev} \quad d\underline{S} = \left(\frac{\delta Q}{T} \right)_{rev}$$

How do we calculate entropy changes?

Example 4.2

Bar of aluminum in ice bath
Current is passed at 1000 W
"Film boiling is occurring at the interface with wispy collapse of the bubbles."



What is the entropy change of the bar, water and the universe per s of operation?

Ans: Ignore actual process, imagine a reversible process for each part of the system:

$$\text{Ice: } \Delta \underline{S}_{ice} = \frac{Q}{T} = + \frac{1000 \text{ J}}{273 \text{ K}} \quad \text{Bar: } \Delta \underline{S} = 0 \text{ (no change!)}$$

$$\text{Universe: } \Delta \underline{S} = \Delta \underline{S}_{ice} = + \frac{1000}{273} \frac{\text{J}}{\text{K}}$$

Example 4.3 (often used as definition of \underline{S} in textbooks)

Two stable equilibrium states of a system, A and B (with different internal constraints); Adiabatic process; Assume irreversible process $A \rightarrow B$

Show that $\Delta \underline{S}_{A \rightarrow B} > 0$

Solution: Develop a reversible process $A \rightarrow B$

Will show that $w_{\text{irrev}}^{A \rightarrow B} > w_{\text{rev}}^{A \rightarrow B}$

Assume for a moment $w_{\text{irrev}}^{A \rightarrow B} \leq w_{\text{rev}}^{A \rightarrow B}$

Perform reverse process: $w_{\text{rev}}^{B \rightarrow A} = -w_{\text{rev}}^{A \rightarrow B}$

Total process: $w_{\text{irrev}}^{A \rightarrow B} - w_{\text{rev}}^{A \rightarrow B} \leq 0$

Contradiction: overall process produced work (thus be first-law balance absorbed heat) with no other change. This is equivalent to case (4) on p. ②.

Then, we must have $0 > w_{\text{irrev}}^{A \rightarrow B} > w_{\text{rev}}^{A \rightarrow B}$

$$0 = Q_{\text{irrev}}^{A \rightarrow B} \quad \left. \begin{array}{l} \\ Q = \Delta \underline{u} - w \end{array} \right\} \Rightarrow Q_{\text{rev}}^{A \rightarrow B} > 0 \Rightarrow \boxed{\Delta \underline{S}^{A \rightarrow B} > 0}$$

FUNDAMENTAL EQUATION

The combined First and Second Laws is the one equation in Thermodynamics to be really remembered:

$$d\underline{s} = \frac{(\delta Q)_{\text{rev}}}{T} = \frac{d\underline{u} - (\delta W)_{\text{rev}}}{T} \Rightarrow \boxed{d\underline{u} = T d\underline{s} - P d\underline{v}}$$

$-(\delta W) = P dV$, if only P work

For open systems, generalize by defining a new property μ , the "Chemical potential" so that:

$$\boxed{d\underline{u} = T d\underline{s} - P d\underline{v} + \sum_i \mu_i dN_i}$$

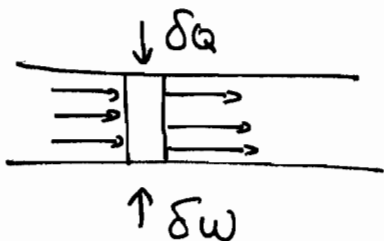
Calculation of $\Delta \underline{s}$ for ideal gases:

$$\Delta \underline{s} (T_1, \underline{v}_1, N \rightarrow T_2, \underline{v}_2, N) = ?$$

$$d\underline{u} = T d\underline{s} - P d\underline{v} \Rightarrow d\underline{s} = \frac{d\underline{u}}{T} + \frac{P d\underline{v}}{T} \quad \frac{P}{T} = \frac{NR}{\underline{v}}$$

$$\Delta \underline{s} = N C_v \ln \frac{T_2}{T_1} + NR \ln \frac{\underline{v}_2}{\underline{v}_1} = N c_p \ln \frac{T_2}{T_1} - NR \ln \frac{P_2}{P_1}$$

For flow systems and reversible process:



$$d\underline{u} = \delta Q + \delta W + h_e d n_e - h_e d n_e \quad [1]$$

at steady-state,

$$d\underline{u} = \phi \quad d n_e = d n_2 = d n \quad (\text{flowing})$$

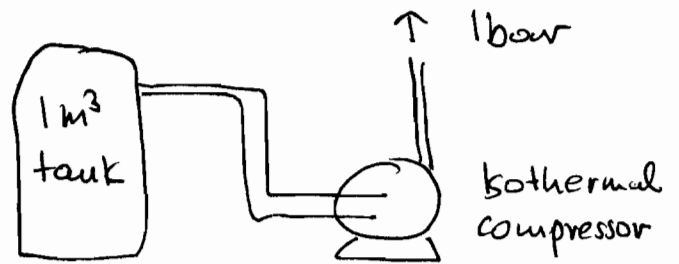
$$[1] \Rightarrow h_2 - h_e = dh = (\delta Q' + \delta W') \quad \because \text{per mole}$$

$$\underline{H} = \underline{u} + P \underline{v} \Rightarrow d\underline{H} = d\underline{u} + P d\underline{v} + \underline{v} dP \Rightarrow dh = T ds + v dP$$

$$\therefore (\delta W')_{\text{rev}} = v dP \Rightarrow (W)_{\text{rev}} = \int_n \int_{P_1}^{P_2} v dP du$$

Example 4.6

$T = 300\text{K}$ at all times
 $P_a = 1\text{ bar}$
 P_t varies



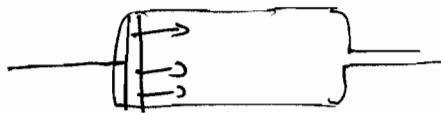
$$dw_\sigma = + dn \int_{P_t}^{P_a} v dP \quad \Rightarrow \quad dw_\sigma = + dn \int_{P_t}^{P_a} \frac{RT}{P} dP = -RT \ln \frac{P_t}{P_a} dy \quad (1)$$

$P_t V = RT$

dn into compressor = - dn out of tank = $-\frac{V_t}{RT} dP_t \Rightarrow \delta w_\sigma = +V_t \ln \frac{P_t}{P_a} dP_t$

$$w_\sigma = +V_t \int_0^1 \ln \frac{P_t}{P_a} dP_t = +V_t \left[P_t \ln \frac{P_t}{P_a} - P_t \right] \Big|_0^1 = +V_t \cdot 1\text{ bar} = +10^5 \text{ J (work done on gas)}$$

We could have guessed the answer!



↑ piston pushing air out

$$w = +P \cdot \Delta V$$