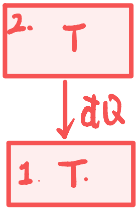
2-3 heat flow between coupled sys.



} reversible.

$$dU = \underline{đQ} + \underline{đW}$$

$$U = U(S, V)$$

$$dU = \underbrace{\frac{\partial U}{\partial S}}_{T} \cdot dS + \underbrace{\frac{\partial U}{\partial V}}_{-P} \cdot dV$$

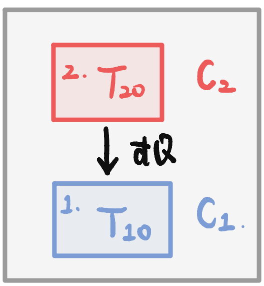
$$\Rightarrow đQ = T \cdot dS \Rightarrow dS = \frac{đQ}{T}$$

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

$$= \frac{đQ}{T_1} + \frac{(-đQ)}{T_2} = 0$$

$$T_1 = T, \quad T_2 = T$$

How about two different temperatures?



$$T_{20} > T_{10}$$

$$dS_1 = \frac{đQ_1}{T_1} = \frac{C_1 \, dT_1}{T_1}$$

1> Energy conservation:

$$\rightarrow \Delta U = 0 = \int_{T_{10}}^{T_f} C_1 dT_1 + \int_{T_{20}}^{T_f} C_2 \cdot dT_2 = 0$$

2> Entropy change:

$$\rightarrow \Delta S_{total} = \underbrace{\int_{T_{10}}^{T_f} \frac{C_1 dT_1}{T_1}}_{\Delta S_1} + \underbrace{\int_{T_{20}}^{T_f} \frac{C_2 dT_2}{T_2}}_{\Delta S_2} \quad ?$$

1> $\to C_1(T_f - T_{10}) + C_2(T_f - T_{20}) = 0$

$\to T_f = \boxed{\dfrac{C_1 T_{10} + C_2 T_{20}}{C_1 + C_2}}$

2> $\to \underbrace{\Delta S}_{\substack{>0 \\ \text{or } =0}} = C_1 \ln \frac{T_f}{T_{10}} + C_2 \ln \frac{T_f}{T_{20}} = \ln \left(\underbrace{\frac{T_f^{\,C_1+C_2}}{T_{10}^{C_1} T_{20}^{C_2}}}_{>1 \text{ or } =1} \right)$

$\left(\dfrac{T_f}{T_{10}^{\frac{C_1}{C_1+C_2}} T_{20}^{\frac{C_2}{C_1+C_2}}} \right)^{C_1+C_2}$

$\underline{T_f}$ vs. $\underline{T_{10}^{\frac{C_1}{C_1+C_2}} T_{20}^{\frac{C_2}{C_1+C_2}}}$

? $>$

It turns out

$\Rightarrow \Delta S_{total} > 0$

*. Heat flow only occurs from high T to low T.

& is irreversible.

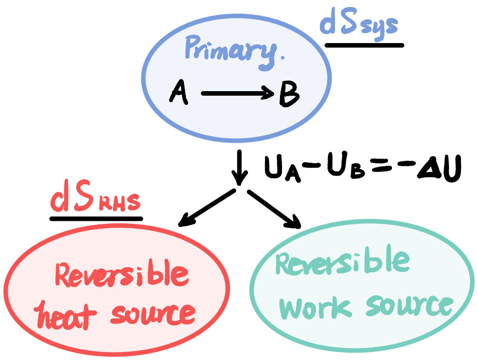
2nd Law of thermodynamics.

*. S of one of subsys could decrease.

whereas the other increases

→ i.e., $\Delta S_{total} > 0$

3. Maximum Work theorem.



*. A → B. delivery of W (Q) is maximized (minimized) for a reversible process.

1> rigid wall	1> Adiabatic wall
2> impermeable.	2> impermeable.
3> Quasi-Static	3> Quasi-Static.

Postulate II : Entropy maximum principle.

$$dS_{total} = dS_{sys} + \underbrace{dS_{RHS}}_{\Downarrow \; \frac{đQ_{RHS}}{T_{RHS}}} \geq 0$$

$$\Rightarrow \quad T_{RHS}\, dS_{sys} + \underline{đQ_{RHS}} \geq 0$$

1> Energy conservation :

$$dU_{sys} + \underline{đQ_{RHS}} + đW_{RWS} = 0$$

$$\Rightarrow \quad T_{RHS}\, dS_{sys} - dU_{sys} - đW_{RWS} \geq 0$$

$$\Rightarrow \quad đW_{RWS} \leq T_{RHS}\, dS_{sys} - dU_{sys}$$

if $\text{đ}W_{RWS} > 0$, then $\text{đ}W_{RWS}$ is maximized at equality sign.

i.e., $dS_{total} = 0$

Furthermore. $\text{đ}W_{RWS} = T_{RHS}\, dS_{sys} - dU_{sys}$

$$= T_{RHS} \frac{\text{đ}Q_{sys}}{T_{sys}} - \underbrace{dU_{sys}}_{(\text{đ}Q_{sys} + \text{đ}W_{sys})}$$

$$\Rightarrow \text{đ}W_{RWS} = T_{RHS} \frac{\text{đ}Q_{sys}}{T_{sys}} - \text{đ}Q_{sys} - \text{đ}W_{sys}$$

$$= \left(1 - \frac{T_{RHS}}{T_{sys}}\right)(-\text{đ}Q_{sys}) + (-\text{đ}W_{sys})$$

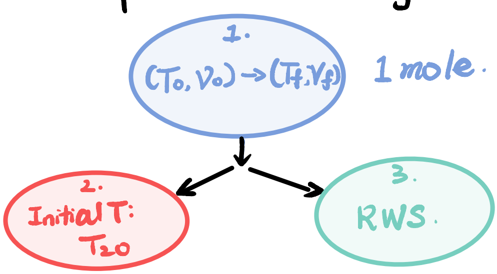
i.e., maximum work comes from

1> a fraction of heat directly extracted from sys.

$\left(1 - \frac{T_{RHS}}{T_{sys}}\right)$

2> the work $(-\text{đ}W_{sys})$ directly extracted from sys.

Example. vdW. Sys.



Q: what's the max work?

Ans: 1> Energy conservation.

$$\Delta U_1 + Q_2 + W_3 = 0$$

2> $\Delta S_{total} = 0 = \Delta S_1 + \Delta S_2$

$\uparrow$

Heat capacity: $C_2(T) = \underset{\text{const.}}{\underset{\downarrow}{D}}T$

For vdW Sys. (see obj #4-4-2)

we know:

$$\begin{cases} S = \underset{1}{\underset{\downarrow}{N}}R\ln[(v-b)(u+a/v)^c] + S_0 \\ \dfrac{1}{T} = \dfrac{cR}{u+a/v} \rightarrow u = cRT - a/v \end{cases}$$

$$\Rightarrow \begin{cases} \Delta S_1 = R\ln\left(\dfrac{V_f - b}{V_0 - b}\right) + cR\ln\dfrac{T_f}{T_0} \\ \Delta U_1 = cR(T_f - T_0) - \left(\dfrac{a}{V_f} - \dfrac{a}{V_0}\right) \end{cases}$$

$\Rightarrow$ For sys 2.

$$Q_2 = \int_{T_{20}}^{T_{2f}} C_2(T)\,dT = \int_{T_{20}}^{T_{2f}} DT\,dT = \frac{1}{2}D(T_{2f}^2 - T_{20}^2)$$

$$\Delta S_2 = \int_{T_{20}}^{T_{2f}} \frac{C_2(T)\,dT}{T} = D(T_{2f} - T_{20})$$

$\Delta S_{total} = \Delta S_1 + \Delta S_2 = 0 \longrightarrow$ max W condition.

$$\rightarrow R\ln\frac{(V_f - b)}{(V_0 - b)} + cR\ln\frac{T_f}{T_0} + D(T_{2f} - T_{20}) = 0$$

$$\rightarrow \underline{T_{2f}} = T_{20} - \frac{R}{D}\ln\left(\frac{V_f - b}{V_0 - b}\right) - \frac{cR}{D}\ln\frac{T_f}{T_0}$$

$$\rightarrow \Delta U_1 + Q_2 + W_3 = 0$$

$$\rightarrow W_3 = -Q_2 - \Delta U_1 = \frac{1}{2}D(T_{20}^2 - \underline{T_{2f}^2}) - cR(T_f - T_0) - \left(\frac{a}{V_f} - \frac{a}{V_0}\right)$$

Max work