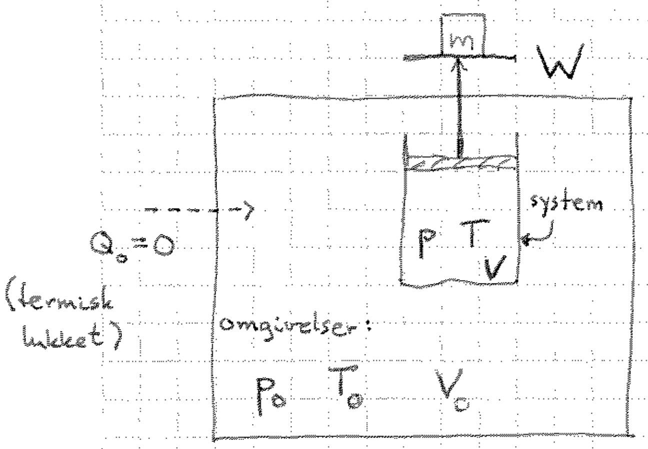
07.03.13

5.3 Eksergi [LHL 17.7]



System + Omgivelser; kan evt. betraktes som to "delsystemer", se eksemplene hedenfor.

Hvis system er i likevekt med omgivelsene, $p = p_0$ og $T = T_0$: Ikke mulig å få ut arbeid.

Hvis system ikke i likevekt med omgivelsene:

Hvor mye arbeid kan vi få ut?

Max. arbeid, eksergi, W_{max} er bestemt ved (tenkt) reversibel prosess mot likevekt:

$$\Delta S_t = \Delta S_0 + \Delta S = 0 \qquad \text{(termisk lukket "totalsystem")}$$

$$\Delta U_t = \Delta U_0 + \Delta U = -W_{max} \qquad \text{(energibevarelse)}$$

$$\Delta V_t = \Delta V_0 + \Delta V = 0$$

samt TDI anvendt på omgivelsene,

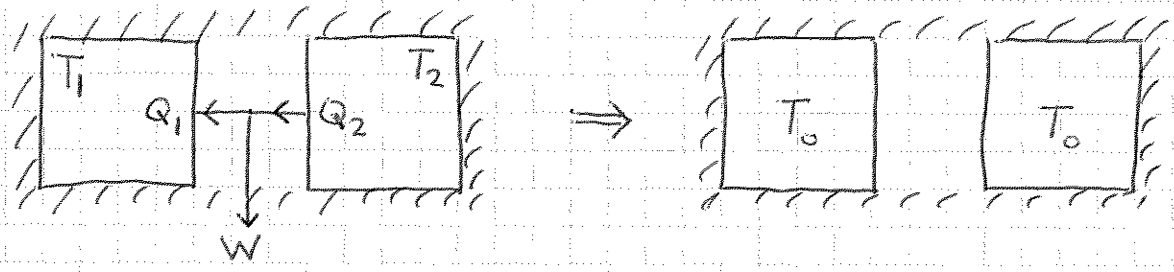
$$T_0 \Delta S_0 = \Delta U_0 + p_0 \Delta V_0$$

gir

$$\begin{aligned} W_{max} &= -\Delta U - \Delta U_0 \\ &= -\Delta U - T_0 \Delta S_0 + p_0 \Delta V_0 \\ &= -\Delta U + T_0 \Delta S - p_0 \Delta V \\ &= -(\Delta U - T_0 \Delta S + p_0 \Delta V) \\ &= -\Delta G \qquad (\text{med } G = U - T_0 S + p_0 V) \end{aligned}$$

= eksergien, det maksimale arbeid som kan trekkes ut ved at systemet (p, T) oppnår likevekt med omgivelsene (p_0, T_0)

Eks 1: Reversibel temperaturutjevning



$T_0 = ?$ $\quad W_{max} = ?$

$$\Delta S_1 = \int_{T_1}^{T_0} \frac{dQ}{T} = \int_{T_1}^{T_0} \frac{C\,dT}{T} = C \ln \frac{T_0}{T_1}$$

$$\Delta S_2 = \int_{T_2}^{T_0} \frac{dQ}{T} = \_\_\_ = C \ln \frac{T_0}{T_2}$$

$\Delta S = \Delta S_1 + \Delta S_2 = 0$ for reversibel prosess i termisk isolert system

$$\Rightarrow \ln \frac{T_0}{T_1} + \ln \frac{T_0}{T_2} = \ln \frac{T_0^2}{T_1 T_2} = 0$$

$$\Rightarrow \underline{T_0 = \sqrt{T_1 T_2}}$$

[Jf. s 59: $T_0 = \frac{1}{2}(T_1 + T_2)$ ved irreversibel temp-utjevning]

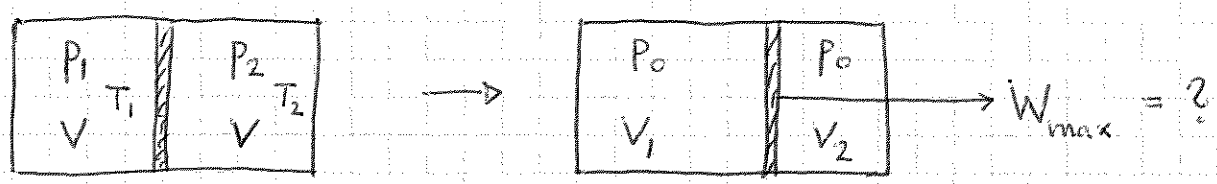
$$W_{max} = -\Delta G = -(\Delta U - T_0 \Delta S + p_0 \Delta V)$$

Her: $\Delta S = 0$, $\Delta V = 0$ $\Rightarrow W_{max} = -\Delta U$

(som stemmer med 1. lov siden $Q = 0$)

$$\begin{aligned} W_{max} &= -\Delta U = -(\Delta U_1 + \Delta U_2) \\ &= -C(T_0 - T_1) - C(T_0 - T_2) \\ &= C(T_1 + T_2 - 2T_0) \\ &= C(T_1 + T_2 - 2\sqrt{T_1 T_2}) \\ &= \underline{C(\sqrt{T_2} - \sqrt{T_1})^2} > 0 \end{aligned}$$

Eks 2: Reversibel trykkutjevning med ideell gass



T_0 (anta $T_1 = T_2 = T_0$)

$$\Delta U = \Delta U_1 + \Delta U_2 = 0 \qquad (\text{da } T_1 = T_2 = T_0)$$

$$\Delta V = \Delta V_1 + \Delta V_2 = 0 \qquad (2V = V_1 + V_2 = \text{konstant})$$

$$\Delta S_1 = n_1 R \ln (V_1 / V)$$

$$\Delta S_2 = n_2 R \ln (V_2 / V)$$

$$W_{max} = \underbrace{-\Delta U}_{=0} + T_0 \Delta S - \underbrace{p_0 \Delta V}_{=0}$$

$$= T_0 (\Delta S_1 + \Delta S_2) = R T_0 \left[n_1 \ln \frac{V_1}{V} + n_2 \ln \frac{V_2}{V} \right]$$

Uttrykt ved (de gitte størrelsene) p_1, p_2 og V:

$$p_1 V = p_0 V_1 = n_1 R T_0 \;, \quad p_2 V = p_0 V_2 = n_2 R T_0$$

$$\Rightarrow (p_1 + p_2) V = p_0 (V_1 + V_2) = 2 p_0 V \quad \Rightarrow p_0 = \tfrac{1}{2}(p_1 + p_2)$$

Slik at

$$\frac{V_1}{V} = \frac{p_1}{p_0} = \frac{2 p_1}{p_1 + p_2} \quad \text{og} \quad \frac{V_2}{V} = \frac{p_2}{p_0} = \frac{2 p_2}{p_1 + p_2}$$

$$\Rightarrow W_{max} = p_1 V \ln \frac{2 p_1}{p_1 + p_2} + p_2 V \ln \frac{2 p_2}{p_1 + p_2}$$

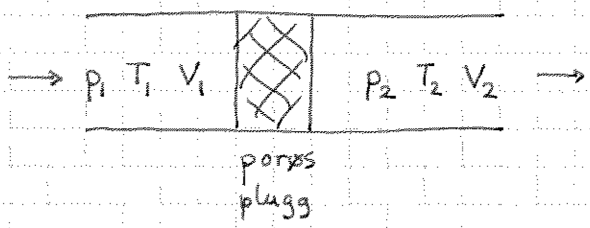
[Som også kan regnes ut direkte:

$$W_{max} = \int_V^{V_1} (p_1 - p_2)\, dV_1 = \int_V^{V_1} p_1 \, dV_1 + \int_V^{V_2} p_2 \, dV_2$$

$$= n_1 R T_0 \ln (V_1 / V) + n_2 R T_0 \ln (V_2 / V) \quad]$$

5.5 Joule-Thomson-effekten [LHL 17.8]

Fra 2.11 :



$H_1 = H_2$ (hvis $Q = 0$)

$(H = U + pV)$

$$\Delta T = \left(\frac{\partial T}{\partial p}\right)_H \Delta p + \left(\frac{\partial T}{\partial H}\right)_p \Delta H \overset{\Delta H = 0}{=} \left(\frac{\partial T}{\partial p}\right)_H \Delta p$$

$\Rightarrow \mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H$ avgjør hva ΔT blir for gitt Δp

Skal vise : $$\boxed{\mu_{JT} = \frac{T\,(\partial V/\partial T)_p - V}{C_p}}$$

[Som er mer hensiktsmessig enn $(\partial T/\partial p)_H$, dvs mer direkte knyttet til tilstandsligningen $f(p, T, V) = 0$]

Bruker "syklisk regel" + "PCH 4.18" :

$$-1 = \underbrace{\left(\frac{\partial T}{\partial p}\right)_H}_{\mu_{JT}} \left(\frac{\partial p}{\partial H}\right)_T \underbrace{\left(\frac{\partial H}{\partial T}\right)_p}_{C_p} \Rightarrow \mu_{JT} = -\frac{(\partial H/\partial p)_T}{C_p}$$

Fra $T\,dS = dU + p\,dV$ utledet vi (se s. 54-55)

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \qquad \text{(PCH 4.18)}$$

Dermed, siden

$$dH = dU + p\,dV + V\,dp = T\,dS + V\,dp,$$

dvs $T\,dS = dH - V\,dp$,

må vi tilsvarende ha (med $U \rightarrow H$ og $p \rightarrow -V$)

$$\left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V \qquad \text{[se evt. s. 74 B]}$$

som gir $\mu_{JT} = C_p^{-1}\left[T(\partial V/\partial T)_p - V\right]$

Utledning av $\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p$:

$$dH = T\,dS + V\,dp$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp \qquad H = H(T,p)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$$

$$dS = \frac{1}{T}dH - \frac{V}{T}dp$$

$$= \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_p dT + \frac{1}{T}\left(\frac{\partial H}{\partial p}\right)_T dp - \frac{V}{T}dp$$

Dermed: $\underbrace{\left(\frac{\partial S}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_p}_{\text{ta } \partial/\partial p}$, $\underbrace{\left(\frac{\partial S}{\partial p}\right)_T = \frac{1}{T}\left(\frac{\partial H}{\partial p}\right)_T - \frac{V}{T}}_{\text{ta } \partial/\partial T}$

$$\Rightarrow \frac{1}{T}\frac{\partial^2 H}{\partial p\,\partial T} = \frac{1}{T}\frac{\partial^2 H}{\partial T\,\partial p} - \frac{1}{T^2}\left(\frac{\partial H}{\partial p}\right)_T + \frac{1}{T^2}\cdot V - \frac{1}{T}\left(\frac{\partial V}{\partial T}\right)_p$$

$$\Rightarrow \left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p \qquad \text{qed}$$