

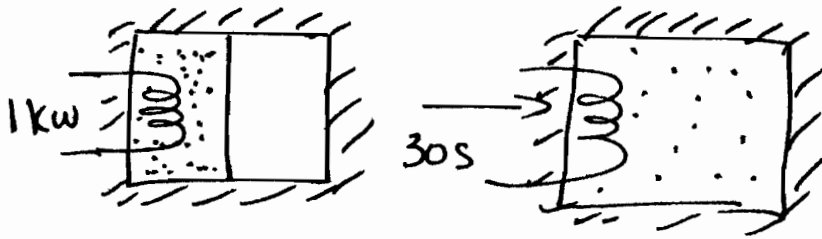
In general, for a reversible process in a closed system, first law balance gives:

$$du = \delta Q^{\text{rev}} + \delta W^{\text{rev}} \Rightarrow \left\{ \begin{array}{l} \text{if} \\ \text{only PV work} \end{array} \right\}$$

$$\boxed{du = Tds - PdV}$$

Fundamental
Equation

Since u, s, v are state functions, this equation is valid for all processes, not just reversible ones.

AS for Ideal Gas (Example 3.3)

$$N = 10 \text{ mol}$$

$$C_v = \frac{5R}{2} = 20.8 \frac{\text{J}}{\text{molK}}$$

$$T_0 = 300 \text{ K}, P_0 = 0.3 \text{ MPa}$$

Closed system: $\Delta u = NC_v \Delta T = W \Rightarrow T_f = T_0 + \frac{W}{NC_v}$

$$= 300 \text{ K} + \frac{1000 \frac{\text{J}}{\text{s}} \cdot 30 \text{ s}}{10 \text{ mol} \cdot 20.8 \frac{\text{J}}{\text{molK}}}$$

$$= 444 \text{ K}$$

$$P_f = P_0 \frac{V_0 T_f}{V_f T_0} = 0.222 \text{ MPa}$$

$\Delta S = \frac{Q_{\text{rev}}}{T}$ is frequently useless / real process is not reversible or const. T.

\Rightarrow Ignore real process, construct reversible path between initial + final states

$$du = Tds - PdV \Rightarrow ds = \frac{1}{T} du + \frac{P}{T} dV \Rightarrow$$

$$\Rightarrow ds = \frac{NC_v}{T} dT + \frac{NR}{V} dV \Rightarrow \boxed{\Delta S = C_v \ln \frac{T_f}{T_0} + R \ln \frac{V_f}{V_0}}$$

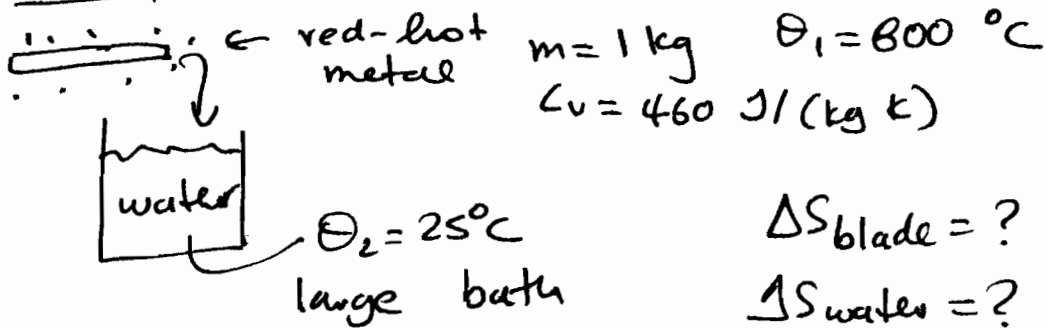
or $ds = \frac{NC_v}{T} dT + \frac{P}{T} \left(-\frac{RT}{P^2} dP + \frac{R}{P} dT \right) = \frac{NC_p}{T} dT - \frac{R}{P} dP$

$$\Rightarrow \boxed{\Delta S = C_p \ln \frac{T_f}{T_0} - R \ln \frac{P_f}{P_0}}$$

In this example, easier to use $\frac{V_f}{V_0}$ (=2) form

$$\Delta S = \frac{5R}{2} \ln \frac{444}{300} + R \ln \frac{2}{1} \Rightarrow \Delta S = 13.9 \frac{\text{J}}{\text{mol K}}$$

Example 3.4 - Forging



Clearly irreversible process \rightarrow ignore

for blade $du = \tau ds - PdV \Rightarrow$

$$ds = \frac{NC_v dT}{T} \Rightarrow \Delta S_{\text{blade}} = NC_v \ln \frac{T_f}{T_0}$$

$$= 1 \text{ kg} \cdot 460 \frac{\text{J}}{\text{kg K}} \cdot \ln \frac{273+25}{273+800} = -589 \frac{\text{J}}{\text{K}}$$

For water - we can obtain the same final state by reversible transfer of

$$Q = -\Delta U_{\text{blade}} = -NC_v \Delta T = -1 \text{ kg} \cdot 460 \frac{\text{J}}{\text{mol K}} \cdot (25 - 800)$$

$$= 356 \text{ kJ}$$

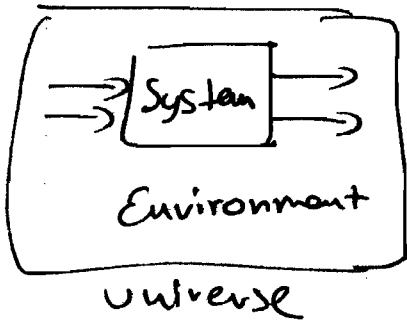
$$\Delta S_{\text{H}_2\text{O}} = \frac{Q}{T} = \frac{356 \text{ kJ}}{(273+25) \text{ K}} = 1196 \frac{\text{J}}{\text{K}}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{blade}} + \Delta S_{\text{water}} = +607 \frac{\text{J}}{\text{K}}$$

Entropy Changes in Open Systems

Entropy is not a conserved quantity; irreversible processes result in entropy increase.

For any process in an open system, we can write an inequality for the entropy change of the universe:



$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{env}$$

$$+ \sum_{\text{leaving streams}} N_{out} S_{out} - \sum_{\text{entering streams}} N_{in} S_{in} \geq 0$$

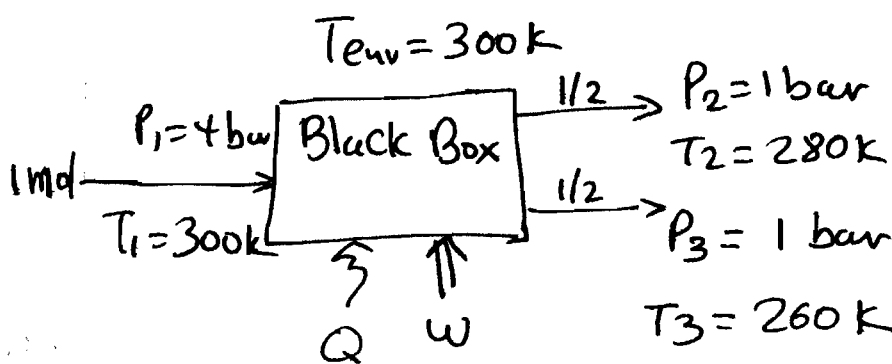
↑
only for reversible processes

(This assumes constant properties of the streams going in + out)

At steady state $\Delta S_{system} = 0$

For adiabatic processes $\Delta S_{env} = 0$

Example 3.5 Feasibility of a process:



$$w = -3.4 \frac{\text{kJ}}{\text{mol}}$$

air; I.G.

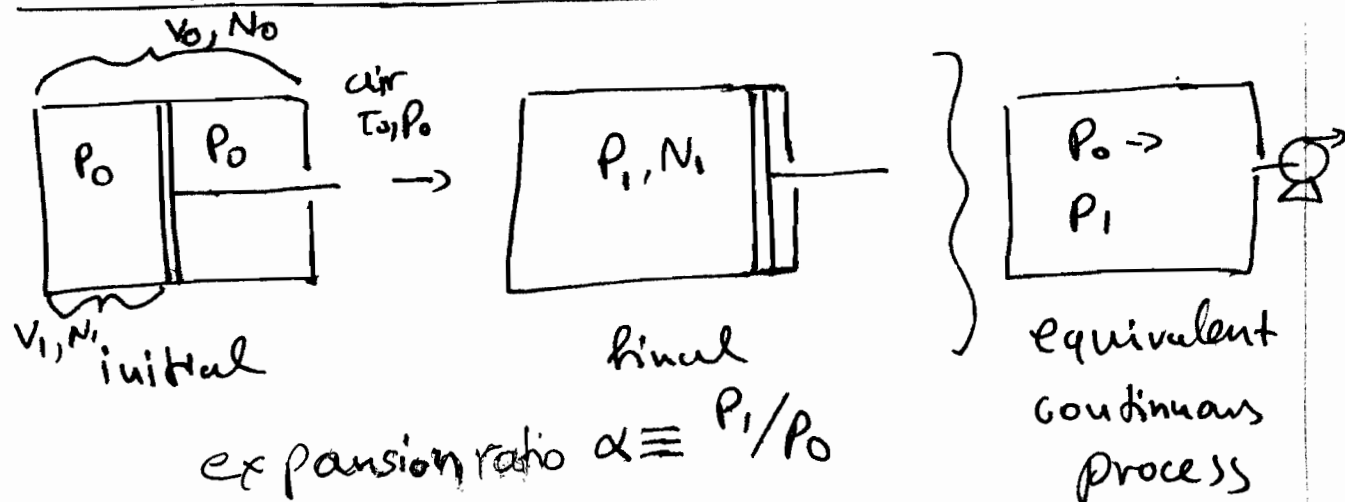
$$C_p = \frac{7R}{2} = 29.1 \frac{\text{J}}{\text{molK}}$$

Is this process feasible?

First Law $\Delta u = 0 = Q + W + N_H_1 - \frac{N_1}{2} H_2 - \frac{N}{2} H_3$
on system
 $\Rightarrow Q = -W - N C_p \left(T_1 - \frac{T_2 + T_3}{2} \right) =$
 $= -(-3400 \text{ J}) - 29.1 \frac{\text{J}}{\text{mol K}} \cdot (300 - 270) = 2527 \text{ J}$
 (heat input)

Second Law $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{env}} +$
on universe
 $+ \frac{N}{2} S_2 + \frac{N}{2} S_3 - N S_1 =$
 $= -\frac{Q}{T_{\text{env}}} + \frac{N}{2} (S_2 - S_1) + \frac{N}{2} (S_3 - S_1) =$
 $= -\frac{Q}{T_{\text{env}}} + \frac{N}{2} \left[C_p \ln \frac{T_2 T_3}{T_1^2} - R \ln \frac{P_2 P_3}{P_1^2} \right] =$
 $= -\frac{2527 \text{ J}}{300 \text{ K}} + \frac{1}{2} \left[29.1 \ln \frac{260 \cdot 280}{300^2} - 8.314 \ln \frac{1}{42} \right] \frac{\text{J}}{\text{K}}$
 $= +0.02 \text{ J/K}$ positive, but very small

Example 3.8 Work for evacuating a tank



Isothermal operation (adiabatic \Rightarrow see book) $T = \text{constant}$

$$\left. \begin{array}{l} \text{init. left: } P_0 V_1 = N_1 RT \\ \text{final: } P_1 V_0 = N_1 RT \\ \text{init total: } P_0 V_0 = N_0 RT \end{array} \right\} \Rightarrow \left. \begin{array}{l} P_0 V_1 = P_1 V_0 \\ \frac{P_1}{P_0} = \frac{N_1}{N_0} \end{array} \right\} \Rightarrow \frac{V_1}{V_0} = \frac{N_1}{N_0} = \alpha$$

$$W = - \int_{V_1}^{V_0} (P - P_0) dV = - \int_{V_1}^{V_0} \frac{N_1 RT}{V} dV + P_0 (V_0 - V_1) =$$

$$= N_1 RT \ln \frac{V_1}{V_0} + P_0 (V_0 - V_1) \Rightarrow$$

$$\frac{W}{N_0} = \frac{N_1}{N_0} RT \ln \frac{V_1}{V_0} + \frac{P_0 V_0}{N_0} - \frac{P_0 V_1}{N_0} = \alpha RT \ln \alpha + RT - \alpha RT$$

$$\Rightarrow \boxed{\frac{W}{RT N_0} = \frac{W}{P_0 V_0} = \alpha \ln \alpha + 1 - \alpha} \quad (1)$$

valid for
both $\alpha \geq 1$
and $\alpha \leq 1$

limit for $\alpha \rightarrow 0$ (complete evacuation)

$$\frac{W}{P_0 V_0} \rightarrow 0 + 1 - \alpha \Rightarrow \boxed{W = P_0 V_0}$$

For $\alpha > 1$ (pressurization) more meaningful measure is work per final mole (mult. (1) by $1/\alpha$)

$$\frac{W}{RT N_1} = \frac{W}{P_1 V_0} = \ln \alpha + \frac{1}{\alpha} - 1$$