Keenan Availabilty

ref: Keenan, Joseph H., Thermodynamics, The MIT Press, paperbook 1970, original J. Wiley & Sons, 1941, QC311K26 1970 Science library

Keenan's definition:

the maximum work which can result from interaction of system and medium when only cyclic changes occur in external things except for the rise of a weight. page 290

medium: environment, atmosphere of infinite extent in which system operates;
- in most stable state
- all parts at rest relative to each other
- homogeneous in temperature and composition
- uniform in pressure at any height in gravitational field

to be shown: $\text{Availability} = \left(E + p_o \cdot V - T_o \cdot S\right) - \left(E_o + p_o \cdot V_o - T_o \cdot S_o\right)$

system at energy E, volume V and entropy S
p_o, T_o pressure and temperature of medium (and of system at dead state - no more possibility of obtaining work)
E_o, V_o, S_o; energy, volume and entropy of system in dead state

first show when exchange of heat can occur between system and medium only, the maximum amount of work which can be delivered beyond the boundaries of the medium when the system changes from one state to another is the work which is delivered when the change is in every respect reversible

assume such process exists: consider complementary reversed process with both rev and irrev - it (irrev) will violate second law

in same way can show same work occurs between any reversible processes

next determine work delivered when system goes from state 1 to 2 ininfinitesimal step δt

$\delta Q = \text{heat\_flow\_TO\_system}$ + if into, - if out of

$\delta W_{\text{state\_change}} = \dfrac{T_o - T}{T} \cdot \delta Q$ from Carnot type cycle

as ... $\delta Q_{med} := T_o \cdot \Delta S$ $\quad \delta Q := T \cdot \Delta S$ $\quad \Delta S := \dfrac{\delta Q}{T}$

$\text{work} := \left(T_o - T\right) \cdot \Delta S$ $\quad \text{work} \rightarrow \left(T_o - T\right) \cdot \dfrac{\delta Q}{T}$

$\delta W > 0$ as both δQ and (To - T) must be same sign

not only work done by system ... volume can expand, etc

any change in volume dV is resisted by the medium with pressure p_o therefore work done by system - the amount of which can be received by things other then the medium is then ...

$\delta W = all\_work\_done\_by\_system$

$\delta W - p_o \cdot dV$ and net work delivered is then ... substitute $\delta W := \delta Q - dE$

$\delta W_{net} := \delta W + \frac{T_o - T}{T} \cdot \delta Q - p_o \cdot dV$ δW_{net} collect, T $\rightarrow -dE - p_o \cdot dV + T_o \cdot \frac{\delta Q}{T}$

δQ cancels $\delta W_{net} = -dE + T_o \cdot \frac{\delta Q}{T} - p_o \cdot dV$

and since process is reversible $\frac{\delta Q}{T} = dS$

$\delta W_{net} = -dE - p_o \cdot dV + T_o \cdot dS$

it follows that the maximum amount of work that can be delivered by each step is then the decrease in ... $E + p_o \cdot V - T_o \cdot S$

maximum decrease is to the dead state $Availability\_at\_state = E + p_o \cdot V - T_o \cdot S - \left(E_o + p_o \cdot V_o - T_o \cdot S_o\right)$ [145]

if system state changes from 1 to 2

increase in availability is ... $E_2 + p_o \cdot V_2 - T_o \cdot S_2 - \left(E_1 + p_o \cdot V_1 - T_o \cdot S_1\right)$ [146]

which is negative unless work or heat is supplied TO the system from a source other than the medium