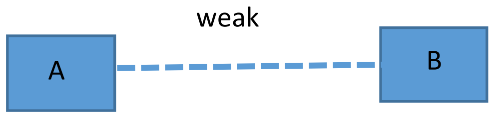
Approach to thermal equilibrium



Total entropy $S^{tot} = S_A(U_A) + S_B(U_T - U_A) \quad U_T = U_A + U_B$

Rate of change $\frac{dS}{dt} = \frac{dU_A}{dt}\frac{\partial S_A}{\partial U_A} + \frac{dU_B}{dt}\frac{\partial S_B}{\partial U_B} = \frac{dU_A}{dt}\left(\frac{\partial S_A}{\partial U_A} - \frac{\partial S_B}{\partial U_B}\right) = \frac{dU_A}{dt}\left(\frac{1}{T_A} - \frac{1}{T_B}\right) > 0$

If $T_A = T_B$ static equilibrium

$T_A > T_B$ need $\frac{dU_A}{dt} < 0$: energy leaves A to go to B. Logical

Now consider S a function of V (volume)

$$S^{tot} = S_A(V_A) + S_B(V_T - V_A)$$

$\frac{dS}{dt} = \frac{dV_A}{dt}\left(\frac{\partial S_A}{\partial V_A} - \frac{\partial S_B}{\partial V_B}\right) = \frac{dV_A}{dt}\left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right) > 0.$

If $P_A > P_B$ and T_A very near T_B, must have $\frac{dV_A}{dt} > 0$. Logical as side with higher pressure expands.

Now let number of particles in A and B be the variables

$$S^{tot} = S_A(N_A) + S_B(N_T - N_A)$$

$$\frac{dS}{dt} = \frac{dN_A}{dt}\left(\frac{\partial S_A}{\partial N_A} - \frac{\partial S_B}{\partial N_B}\right) = -\frac{dN_A}{dt}\left(\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B}\right) > 0$$

Where we have defined a chemical potential : $\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$

If $\mu_A > \mu_B$ need $\frac{dN_A}{dt} < 0$ side with high chemical potential loses particles.

μdN analogous to chemical work

General $dS = \left(\frac{\partial S}{\partial U}\right)_{V.N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN = \frac{dU}{T} + \frac{P}{T}dV - \frac{\mu}{T}dN$