

Equilibrium macrostate has the highest $\ln\Omega$, hence

$$\begin{aligned} \frac{d\ln\Omega_{\text{total}}}{d\epsilon_{\text{LHS}}} &= 0 \\ \therefore \frac{d(\ln\Omega_{\text{LHS}} + \ln\Omega_{\text{RHS}})}{d\epsilon_{\text{LHS}}} &= 0 \\ \therefore \frac{d\ln\Omega_{\text{LHS}}}{d\epsilon_{\text{LHS}}} + \frac{d\ln\Omega_{\text{RHS}}}{d\epsilon_{\text{LHS}}} &= 0 \end{aligned}$$

Since:

$$\begin{aligned} \epsilon_{\text{total}} &= \epsilon_{\text{LHS}} + \epsilon_{\text{RHS}} = \text{constant} \\ \therefore d\epsilon_{\text{LHS}} &= -d\epsilon_{\text{RHS}} \\ \therefore \frac{d\ln\Omega_{\text{LHS}}}{d\epsilon_{\text{LHS}}} &= \frac{d\ln\Omega_{\text{RHS}}}{d\epsilon_{\text{RHS}}} \end{aligned}$$

Since $S = k_B \ln\Omega$

$$\frac{dS_{\text{LHS}}}{d\epsilon_{\text{LHS}}} = \frac{dS_{\text{RHS}}}{d\epsilon_{\text{RHS}}}$$

Intuitively, equilibrium implies equal “temperature” for the ensembles. Combined with dimensional arguments ($[S]/[\epsilon] = K^{-1}$) suggests

$$\frac{dS}{d\epsilon} = \frac{1}{T} \text{ for any system}$$

Since we considered the energy levels to be fixed, implicitly we assumed $V = \text{const.}$ (QM predicts energy spacing increases as size of potential well decreases), hence formally

$$\underline{\left(\frac{\partial S}{\partial \epsilon} \right)_V = \frac{1}{T}}$$

Classically:-

Expect $U = U(T)$ for an ideal gas, but Joule found slight cooling during isoenergetic expansion of a real gas. Suggests we need other variables to fully define U .

Fundamental thermodynamic relationship:

$$dU = TdS - pdV$$

c.f (PHY1116) for a general function $f(x,y)$:

$$df(x, y) = \left(\frac{\partial f(x, y)}{\partial x} \right)_y dx + \left(\frac{\partial f(x, y)}{\partial y} \right)_x dy$$

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

$$\left(\frac{\partial U}{\partial S} \right)_V = T \quad \left(\frac{\partial U}{\partial V} \right)_S = -p$$

Hence (first relation) :

$$\left(\frac{\partial S}{\partial U} \right)_V = \frac{1}{T} \quad \text{c.f.} \quad \left(\frac{\partial S}{\partial \epsilon} \right)_V = \frac{1}{T} \quad \text{found earlier}$$

S & V are the “natural variables” of U .