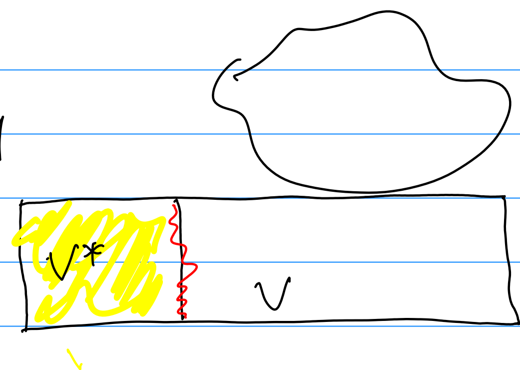
Entropy

- thermodynamic entropy 1 mole of ideal gas

$\{p, v, \theta, S\}$



$$dU = p\,dv - \theta\,dS$$

$$pV = R\theta$$

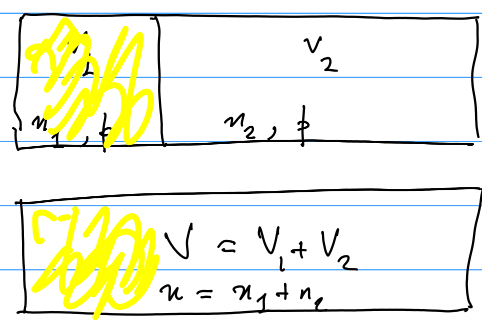
expand isothermally, quasistatically   no change in U

$$0 = \int_{V^*}^{V} dU = \int_{V^*}^{V} p\,dV - \theta \int_0^{\Delta S} dS$$

$$= \int_{V^*}^{V} R\theta \frac{dV}{V} - \theta \int_0^{\Delta S} dS$$

$$\Delta S = R \log \frac{V}{V^*} = -R \log \frac{V^*}{V}$$

2. Entropy of Mixing



$$U_1 = pV_1 n_1 \qquad U_2 = pV_2 n_2$$

$$pV_1 = n_1 R\theta \qquad pV_2 = n_2 R\theta$$

$p_{new} = p_1 + p_2$

p_1 = partial pressure of Gas 1

p_2 = partial pressure of Gas 2

$$p_{new} = p_1 + p_2 = \frac{n_1 R\theta}{V} + \frac{n_2 R\theta}{V}$$

Dalton's Law

(extra thermodynamical hypothesis)

$$= \frac{R\theta}{V}(n_1 + n_2)$$

$$= \frac{R\theta}{V}\left(\frac{pV_1}{R\theta} + \frac{pV_2}{R\theta}\right)$$

$$= p$$

$$p_{new} = p$$

$$\Delta S_1 = -n_1 R \log \frac{V_1}{V}, \qquad \Delta S_2 = -n_2 R \log \frac{V_2}{V}$$

$$\Delta S = -R\left(n_1 \log \frac{n_1}{n_1 + n_2} + n_2 \log \frac{n_2}{n_1 + n_2}\right)$$ entropy of mixing

proportional to configurational entropy with probabilities

$$p_1 = \frac{n_1}{n}, \quad p_2 = \frac{n_2}{n} \qquad n = n_1 + n_2$$

Configurational entropy
(change the sign)
negative of Shannon entropy

$$\Phi(p) = \underbrace{\sum_{k=1,\dots,r} p_k \log p_k}_{\leqq 0} \qquad \sum p_k = 1, \; p_k \geqq 0 \qquad 0 \cdot \log 0 = 0$$

$$X = \{x_1, \dots, x_r\} \qquad \mathrm{Prob}(\omega_i = x_k) = p_k, \quad k = 1, \dots, r$$

$$\log \frac{1}{r} \leqq \Phi(p) \leqq 0$$

minimum of Φ: $p_k = \frac{1}{r}$ uniform distribution $\Phi = \log \frac{1}{r}$
"most random"

maximum of Φ: $p_k = 1$ for one k, $p_n = 0$ otherwise $\Phi = 0$
least random
x_k occurs and no others

Suppose p^*, p dependent
successive distributions of a Markov chain

$$P = (p_{ij})$$

$$p = p^* P$$

$$p(x_i, x_j) = p_i^* p_{ij}$$

$$\Phi(p(x_i, x_j)) = \sum p(x_i, x_j) \log p(x_i, x_j)$$

$$= \sum p_i^* p_{ij} \log p_i^* p_{ij}$$

$$= \sum p_i^* p_{ij} \log p_i^* + \sum p_i^* p_{ij} \log p_{ij}$$

$$= \Phi(p^*) + \sum p_i^* \Phi_i(P)$$

entropy of i^{th} row of P

$$\Phi(x|x_i) = \sum p(x_j|x_i) \log p(x_j|x_i)$$

$$p_j \log p_j = \sum_i p_i^* p_{ij} \log\left(\sum_i p_i^* p_{ij}\right) \leq \sum p_i^* p_{ij} \log p_{ij}$$

sum on j Jensen

$$\Phi(p) \leq \sum p_i^* \Phi_i(P)$$

$$\Phi(p(x_i, x_j)) \geq \Phi(p^*) + \Phi(p)$$

conditioning reduces uncertainty !