

P+V loop

1. Along the adiabat we need $PV^\gamma = \text{const}$; at ~~the~~ the ends, therefore,

$$(3P_0) V_0^{5/3} = P_0 (8V_0)^{5/3}, \text{ or } \boxed{\beta = 32}$$

2. Isobaric leg:

$$W = -\int P dV = -P_0 \int_{8V_0}^{V_0} dV = -P_0 (V_0 - 8V_0) = 7P_0 V_0.$$

$$\Delta U = \frac{3}{2} NK\Delta T \quad \text{but} \quad P_0 \Delta V = NK\Delta T, \text{ so}$$

$$\Delta U = \frac{3}{2} P_0 \Delta V = \frac{3}{2} P_0 (V_0 - 8V_0) = -\frac{3}{2} \cdot 7P_0 V_0.$$

$$Q = \Delta U - W = -\frac{3}{2} \cdot 7P_0 V_0 - 7P_0 V_0 = -\frac{5}{2} \cdot 7P_0 V_0.$$

$$dQ = dU - dW = \frac{3}{2} P_0 dV + P_0 dV = \frac{5}{2} P_0 dV, \text{ so}$$

$$ds = \frac{dQ}{T} = \frac{5/2 P_0 dV}{T} \quad \text{but} \quad P_0 V = NK T \rightarrow \frac{1}{T} = \frac{NK}{P_0 V}$$

$$= \frac{5}{2} \frac{P_0 dV}{P_0 V} \cdot NK = \frac{5}{2} NK \frac{dV}{V}, \text{ so}$$

$$\begin{aligned} \Delta S &= \int_{8V_0}^{V_0} ds = \frac{5}{2} NK \int_{8V_0}^{V_0} \frac{dV}{V} = \frac{5}{2} NK \ln(V_0/8V_0) \\ &= -\frac{5}{2} NK \ln 8 \end{aligned}$$

So Isobaric leg has

$$W = 7P_0 V_0; \quad \Delta U = -\frac{3}{2} \cdot 7P_0 V_0; \quad Q = -\frac{5}{2} \cdot 7P_0 V_0$$

$$\Delta S = -\frac{5}{2} NK \ln 8 = -\frac{15}{2} NK \ln 2$$

(2)

Iso volumetric leg:

$$W = 0$$

$$\begin{aligned}\Delta U &= \frac{3}{2} Nk \Delta T = \frac{3}{2} \Delta P \cdot V_0 = \frac{3}{2} (32P_0 - P_0) \cdot V_0 \\ &= \frac{3}{2} \cdot 31 P_0 V_0\end{aligned}$$

$$Q = \Delta U - W = \frac{3}{2} 31 P_0 V_0$$

$$ds = \frac{dQ}{T} = \frac{dU}{T} = \frac{\frac{3}{2} Nk dT}{T} = \frac{\frac{3}{2} V_0 dP}{T}$$

$$= \frac{3}{2} \frac{V_0 dP}{P \cdot V_0} \cdot Nk = \frac{3}{2} Nk \frac{dP}{P}, \text{ so}$$

$$\Delta S = \int_{P_0}^{32P_0} ds = \int_{P_0}^{32P_0} \frac{3}{2} Nk \frac{dP}{P} = \frac{3}{2} Nk \ln P \Big|_{P_0}^{32P_0}$$

$$= \frac{3}{2} Nk \ln 32 = \frac{15}{2} Nk \ln 2$$

So Iso volumetric leg has

$$W = 0; \quad \Delta U = \frac{3}{2} \cdot 31 P_0 V_0; \quad Q = \frac{3}{2} 31 P_0 V_0$$

$$\Delta S = \frac{15}{2} Nk \ln 2.$$

Adiabatic leg: $PV^{5/3} = 32P_0V_0^{5/3} = 32P_0 \frac{V_0^{5/3}}{8V_0}$, \rightarrow

(3)

$$\begin{aligned}
 W &= - \int P dV = -32P_0V_0^{5/3} \int_{V_0}^{8V_0} \frac{dV}{V^{5/3}} \\
 &= -32P_0V_0^{5/3} \left(-\frac{3}{2} V^{-2/3} \Big|_{V_0}^{8V_0} \right) = +32P_0V_0^{5/3} \cdot \frac{3}{2} \left(\frac{1}{(8V_0)^{2/3}} - \frac{1}{V_0^{2/3}} \right) \\
 &= 32P_0V_0^{5/3} \cdot \frac{3}{2} \frac{1}{V_0^{2/3}} \left(\frac{1}{4} - 1 \right) \\
 &= -\frac{3}{4} \left(\frac{3}{2} \right) 32P_0V_0^{5/3} = -36P_0V_0.
 \end{aligned}$$

$$\begin{aligned}
 \Delta U &= \frac{3}{2} Nk\Delta T = \frac{3}{2} (P_0(8V_0) - (32P_0)(V_0)) \\
 &= \frac{3}{2} P_0V_0(8-32) = -36P_0V_0
 \end{aligned}$$

$$Q = 0 \quad \checkmark \quad \Delta S = 0$$

Iso adiabatic leg has

$$W = -36P_0V_0; \quad \Delta U = -36P_0V_0; \quad Q = \Delta S = 0.$$

3. All told, then,

$$\begin{aligned}
 \Delta U &= \Delta U_{\text{isobaric}} + \Delta U_{\text{isovolumetric}} + \Delta U_{\text{adiabatic}} \\
 &= -\frac{21}{2} P_0V_0 + \frac{93}{2} P_0V_0 + -36P_0V_0 \\
 &= \left(\frac{72}{2} - 36 \right) P_0V_0 = 0 \quad \checkmark
 \end{aligned}$$

$$\begin{aligned}
 \Delta S &= \Delta S_{\text{isobaric}} + \Delta S_{\text{isovolumetric}} + \Delta S_{\text{adiabatic}} \\
 &= -\frac{15}{2} Nk \ln 2 + \frac{15}{2} Nk \ln 2 + 0 = 0 \quad \checkmark
 \end{aligned}$$

4. The net work on the gas is

$$W_{\text{net}} = W_{\text{isobaric}} + W_{\text{isovolumetric}} + W_{\text{adiabatic}}$$
$$= 7P_0V_0 + 0 + -36P_0V_0 = -29P_0V_0.$$

The work done by the gas is $-1 \times$ this:

$$W = 29 P_0 V_0$$

Q_{in} is the heat absorbed during the isovolumetric leg:

$$Q_{\text{in}} = \frac{93}{2} P_0 V_0$$

So the efficiency is

$$\frac{W}{Q_{\text{in}}} = \frac{29 P_0 V_0}{\frac{93}{2} P_0 V_0} = \frac{58}{93} = \text{efficiency}$$

Langmuir adsorption

1. The surface has N sites, of which n are occupied. This can be accomplished in $\binom{N}{n}$ ways, so

$$\Omega = \frac{N!}{n!(N-n)!}$$

2. Each n bound atom gets a ~~big~~ binding energy $-E = -10kT$, so

$$G_{\text{binding}} = -n(10kT) - kT \ln \frac{N!}{n!(N-n)!}$$
$$= -n10kT - kT \ln N! + kT \ln n! + kT \ln (N-n)!$$

$$\mu_{\text{binding}} = \frac{\partial G}{\partial n} = -10kT + kT \ln n - kT \ln (N-n)$$

$$= -10kT + kT \ln \frac{n}{N-n} \approx -10kT + kT \ln \frac{n}{N} \text{ if } n \ll N.$$

Meanwhile, for the ideal gas,

$$\mu = -kT \ln \left(\frac{V}{N} \frac{1}{V_Q} \right) \quad \text{or} \quad V_Q = \left(\frac{h^2}{2\pi m_A kT} \right)^{3/2}$$
$$= kT \ln(N/V) + kT \ln V_Q$$

Setting the chemical potentials equal (at equilibrium):

$$\mu_{\text{binding}} = \mu$$

$$-10kT + kT \ln \frac{n}{N} = kT \ln \left(\frac{N}{V} \cdot \frac{V_Q}{V} \right)$$

$$e^{-10} \cdot \frac{n}{N} = \frac{N}{V} \cdot V_Q$$

$$\frac{n}{N} = \frac{N}{V} \cdot V_H \frac{1}{40^{3/2}} \cdot e^{10} = \left(\frac{10^{-23} N_A}{10^{-25} m^3} \right) 10^{-30} \frac{1}{40^{3/2}} e^{10} = \boxed{5.2 \times 10^{-5}}$$

$$= \left(\frac{h^2}{2\pi m_H kT} \right)^{3/2} \left(\frac{m_H}{m_A} \right)^{3/2}$$

$$= V_H \cdot \left(\frac{1}{40} \right)^{3/2}$$

$$= (1.01 \text{ \AA})^3 \cdot \frac{1}{40^{3/2}}$$

Triple point

(1)

From the Clausius - Clapeyron relation, $\frac{dp}{dT} = \frac{\Delta S}{\Delta V}$ along the phase boundary, so

$$\Delta S_{gs} = \Delta S_{ge} + \Delta S_{es} \quad (\Delta S_{gs} \equiv S_g - S_s, \text{ etc})$$

so

$$\frac{\Delta S_{gs}}{\Delta V_{gs}} = \frac{\Delta V_{ge}}{\Delta V_{gs}} \frac{\Delta S_{ge}}{\Delta V_{ge}} + \frac{\Delta V_{es}}{\Delta V_{gs}} \frac{\Delta S_{es}}{\Delta V_{es}}, \text{ or}$$

$$\left(\frac{dp}{dT}\right)_{gs} = \frac{\Delta V_{ge}}{\Delta V_{gs}} \left(\frac{dp}{dT}\right)_{ge} + \frac{\Delta V_{es}}{\Delta V_{gs}} \left(\frac{dp}{dT}\right)_{es}$$

~~$V_g = RT/p_g$~~ $V_e = \mu/p_e$ and $V_s = \mu/p_s$, but

for the gas $V_g = RT/p_0$, so

$$\frac{\Delta V_{ge}}{\Delta V_{gs}} = \frac{V_g - V_e}{V_g - V_s} = \frac{RT/p_0 - \mu/p_e}{RT/p_0 - \mu/p_s} = \frac{p_e \cdot RT/\mu p_0 - 1}{p_e RT/\mu p_0 - p_e/p_s}$$

$$\text{so } \frac{\Delta V_{ge}}{\Delta V_{gs}} = \frac{\alpha - 1}{\alpha - \beta}$$

$$\text{Similarly, } \frac{\Delta V_{es}}{\Delta V_{gs}} = \frac{V_e - V_s}{V_g - V_s} = \frac{\mu/p_e - \mu/p_s}{RT/p_0 - \mu/p_s} = \frac{1 - \beta}{\alpha - \beta}, \text{ so}$$

$$\left(\frac{dp}{dT}\right)_{gs} = \left(\frac{\alpha - 1}{\alpha - \beta}\right) \left(\frac{dp}{dT}\right)_{ge} - \left(\frac{\beta - 1}{\alpha - \beta}\right) \left(\frac{dp}{dT}\right)_{es}$$

Putting in numbers,

$$\rho_l = 1.00 \text{ g/cm}^3$$

$$\rho_s = 0.92 \text{ g/cm}^3$$

$$R = 8.3 \text{ J/K/mole}$$

$$T = 273 \text{ K}$$

$$\mu = 18 \text{ g/mole}$$

$$P_0 = 611 \text{ N/m}^2$$

$$\alpha \equiv \frac{\rho_l R T}{\mu P_0} = \left(\frac{1.00 \text{ g}}{\text{cm}^3} \right) \left(\frac{8.3 \text{ J}}{\text{K} \cdot \text{mole}} \right) (273 \text{ K}) \left(\frac{\text{mole}}{18 \text{ g}} \right) \left(\frac{\text{m}^2}{611 \text{ N}} \right)$$

$$= 0.21 \frac{\text{J m}^2}{(\text{mole}) \text{cm}^3} \times \left(\frac{10^2 \text{ cm}}{\text{m}} \right)^3 = 2.1 \times 10^5$$

$$\beta \equiv \frac{\rho_l}{\rho_s} = \frac{1.00}{0.92} = 1.09$$

$$\frac{\alpha - 1}{\alpha - \beta} \approx 1$$

$$\frac{1 - \beta}{\alpha - \beta} \approx \frac{1 - \beta}{\alpha} = \frac{0.09}{2.1 \times 10^5} = 4.5 \times 10^{-7}, \text{ so}$$

$$\left(\frac{dp}{dT} \right)_{gs} = \left(\frac{dp}{dT} \right)_{gl} - (4.5 \times 10^{-7}) \left(\frac{dp}{dT} \right)_{ls}$$

Looking at the phase diagram,

$$\left(\frac{dp}{dT} \right)_{gs} \approx \left(\frac{dp}{dT} \right)_{gl}, \text{ although the gs has a slightly}$$

longer slope; this agrees w/ my expression above b/c

$\left(\frac{dp}{dT} \right)_{ls} < 0$, so we expect $\left(\frac{dp}{dT} \right)_{gs} > \left(\frac{dp}{dT} \right)_{gl}$. The prefactor

for the ls slope is 10^{-7} , so we'd expect its contribution to be negligible except for cases like water where $\left(\frac{dp}{dT} \right)_{ls}$ is huge.