$$dS = \underbrace{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}_{T_1 = T_2} dU_1 + \underbrace{\left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right)}_{P_1 = P_2} dV_1 + \underbrace{\left(\frac{\mu_2}{T_2} - \frac{\mu_1}{T_1}\right)}_{\mu_2 = \mu_1} dN_1 = 0$$

—

$dV_1 = 0$; $dN_1 = 0$

$$dS = \underbrace{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}_{>0} \underbrace{dU_1}_{>0} \geqslant 0$$

Se $dU_1 > 0$, $T_1 < T_2$ → A energia flui do subsistema a temperatura mais elevada para o subsistema a temp. mais baixa.

$dU_1 = 0$, $dV_1 = 0$

$$dS = \frac{1}{T} \underbrace{(\mu_2 - \mu_1)}_{>0} \underbrace{dN_1}_{>0} \geqslant 0$$

$\mu_2 > \mu_1$ $dN_1 > 0$ ⇒ partículas fluem para subs.

82.

$U = a V T^4$

a) $C_V = ?$ $\quad C_V = \left(\frac{\partial U}{\partial T}\right)_V = 4 a V T^3$

$\lim_{T \to 0} C_V = 0$ (3ª Lei) ✓

$dU = T dS - P dV$
Dividindo por dT a $V =$ cte,
$$\underbrace{\left(\frac{\partial U}{\partial T}\right)_V}_{C_V} = T \left(\frac{\partial S}{\partial T}\right)_V + 0$$

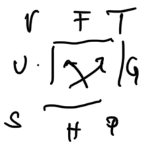
b) $S = S(V,T)$ $\quad C_V dT = T dS$

$$S(V,T) = \int_0^T \frac{C_V(T)}{T} dT \qquad (S(V, T=0) = 0,\ 3^a \text{ Lei})$$

$$= \int_0^T \frac{4 a V T^3}{T} dT = \int_0^T 4 a V T^2 dT = \frac{4}{3} a V T^3 \qquad \boxed{\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}}$$

c) $F = U - TS$

$$= a V T^4 - T \cdot \frac{4}{3} a V T^3 = -\frac{1}{3} a V T^4$$



d) $P = P(V,T)$ $\quad P = -\left(\frac{\partial F}{\partial V}\right)_T = -\frac{\partial}{\partial V}\left[-\frac{1}{3} a V T^4\right]_T = \frac{1}{3} a T^4$

$P = \frac{1}{3} \frac{U}{V}$

$$\frac{U}{V} = \frac{a V T^4}{V} = a T^4 \rightarrow P = \frac{1}{3} \frac{U}{V} \ ✓ \quad \left[\text{gás ideal: } P = \frac{2}{3} \frac{U}{V}\right]$$

e) $P V^{4/3} =$ cte

$S = cte$, $\underbrace{\frac{4}{3} a V T^3 = cte}$; $P = \frac{1}{3} a T^4$; $T^3 = P^{3/4} \left(\frac{3}{a}\right)^{3/4}$

$VT^3 = cte$ $\quad VP^{3/4}\left(\frac{3}{a}\right)^{3/4} = cte$; $VP^{3/4} = cte \Rightarrow PV^{4/3} = cte$

[gás ideal: $PV^{\gamma} = cte$]

91. $S = S(V,T)$

Gás ideal: $S(V,T) = nC_V \ln(T) + nR\ln(V) + cte$

$$\Delta S = nC_V \ln\left(\frac{T_f}{T_i}\right) + nR\ln\left(\frac{V_f}{V_i}\right)$$

$$dS = \underline{\left(\frac{\partial S}{\partial V}\right)_T} dV + \underline{\left(\frac{\partial S}{\partial T}\right)_V} dT$$

$$\frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V} \quad ; \quad \frac{\partial}{\partial V}\left(-S\right)_T = \frac{\partial}{\partial T}\left(-P\right)_V$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

$$dS = \underline{\left(\frac{\partial P}{\partial T}\right)_V} dV + \frac{C_V}{T} dT$$

Van der Waals: $\left(P + \frac{a n^2}{V^2}\right)(V - nb) = n$

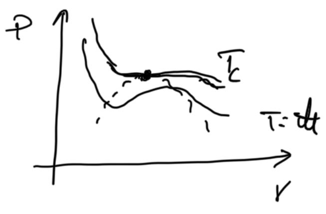
$$\underbrace{P = \frac{nRT}{(V-nb)} - \frac{a n^2}{V^2}}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V-nb} \quad ; \quad dS = \frac{nR}{V-nb} dV + \frac{C_V}{T} dT$$

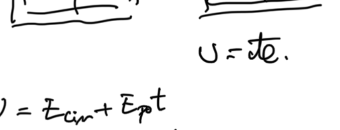
$$\int_i^f dS = \Delta S = S_f - S_i = \int_{V_i}^{V_f} \frac{nR}{V-nb} dV + \int_{T_i}^{T_f} \frac{C_V}{T} dT = nR\ln\left(\frac{V_f - nb}{V_i - nb}\right) + C_V \ln\left(\frac{T_f}{T_i}\right)$$

92. $\left(\frac{\partial P}{\partial V}\right)_T = 0$; $\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$

(...)



93. Queremos calcular $\underline{\left(\frac{\partial T}{\partial V}\right)_U}$



U = cte.

$U = U(T,V)$

Gás real: $U = E_{cin} + \underbrace{E_{pot}}_{<0}$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$= C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \equiv 0$$

Na expansão $|E_{pot}|$ diminui

E_{cin} diminui $\Rightarrow$ T diminui?

$$C_V\, dT = -\left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left(\frac{\partial U}{\partial V}\right)_T$$

$dU = T\,dS - P\,dV$

Dividindo por dV, mantendo $T =$ cte,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\underbrace{\left(\frac{\partial S}{\partial V}\right)_T}_{\left(\frac{\partial P}{\partial T}\right)_V} - P$$

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]$$

Gás ideal: $P = \frac{nRT}{V}$, $\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V} = \frac{P}{T} \to \left(\frac{\partial T}{\partial V}\right)_U = 0$

Gás de van der Waals: $\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V-nb}$

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left[\frac{nRT}{V-nb} - \left(\frac{nRT}{V-nb} - \frac{an^2}{V^2}\right)\right] = -\frac{1}{C_V}\frac{an^2}{V^2}$$

$$\Delta T = -\int_{V_i}^{V_f}\frac{1}{C_V}\frac{an^2}{V^2}\,dV \underset{\substack{\text{assumindo}\\ C_V = \text{cte}}}{=} -\frac{a}{C_V}n^2\left[\frac{1}{V_i} - \frac{1}{V_f}\right] = \frac{a}{C_V}n^2\left[\frac{1}{V_f} - \frac{1}{V_i}\right]$$

$V_f > V_i$; $\Delta T < 0$

94.

a) Resolvido no compêndio :)

89. $U(V,T) = u(T)\,V$; $P = u(T)\frac{1}{3}$; $\mu = 0$

a) $dU = T\,dS - P\,dV \to \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$

b) $\mu = \left(\frac{\partial G}{\partial N}\right)_{P,T}$

P, T e μ são variáveis intensivas

G e N extensivas ; $G = N\underbrace{g(T,P)}_{\text{energia livre de Gibbs por partícula}}$

$\mu = g(T,P)$:) $\mu = \frac{G}{N}$

c) $S(V,T) = \frac{4}{3}\frac{u(T)}{T}V$; $S(V,T=0) = S(V=0,T) = 0$

i) $\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left(\frac{\partial U}{\partial V}\right)_T + \frac{P}{T}$; $\left(\frac{\partial U}{\partial V}\right)_T = u(T)$; $\frac{P}{T} = \frac{u(T)}{3T}$

$$\underline{\left(\frac{\partial S}{\partial V}\right)_T} = \frac{u(T)}{T} + \frac{1}{3}\frac{u(T)}{T} = \frac{4}{3}\frac{u(T)}{T}$$

$$S(V,T) = \frac{4}{3}\frac{u(T)}{T}V + f(T) \quad ; \qquad S(V=0,T)=0 \rightarrow f(T)=0$$

$$S(V,T) = \frac{4}{3}\frac{u(T)}{T}V$$

ii) $G = ?$ $\qquad (\mu = 0 \Rightarrow G = 0)$

$$G = U + PV - TS = \underbrace{u(T)V}_{U} + \underbrace{\frac{u(T)}{3}}_{P} \times V - T \times \frac{4}{3}\frac{u(T)}{T}V$$

$$= \frac{4}{3}u(T)V - \frac{4}{3}u(T)V \equiv 0$$

iii) $C_V = 3S$

$U = U(P,V) \qquad U = u(T)V = \underbrace{3P}_{u(T)}V = 3PV$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3\underbrace{\left(\frac{\partial P}{\partial T}\right)_V}_{\left(\frac{\partial S}{\partial V}\right)_T} V = 3 \times \frac{\partial}{\partial V}\underbrace{\left(\frac{4}{3}\frac{u(T)}{T}V\right)_T}_{S} V$$

$$= 4\frac{u(T)}{T}V = 3 \times \underbrace{\frac{4}{3}\frac{u(T)}{T}V}_{S} = 3S.$$

iv) $C_P = ?$ $\qquad (dQ)_P = \underbrace{C_P}_{\infty}\,\underbrace{dT}_{0} \qquad P = \frac{1}{3}u(T) \equiv \underbrace{P(T)}$

A pressão constante, não conseguimos variar a temperatura!

C_P não está definido ... Formalmente $C_P \to \infty$

—•—