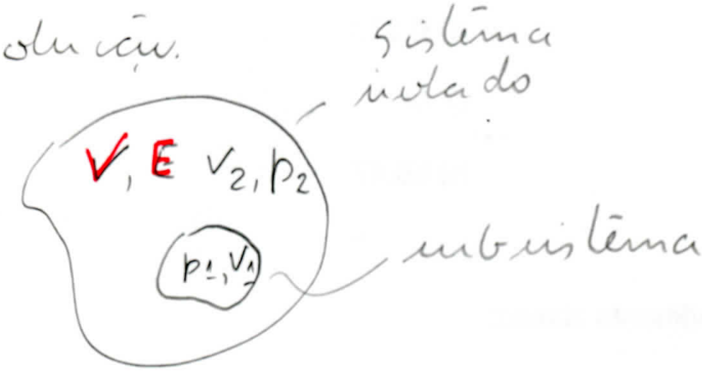
Problema 1).

Demonstrar que, num <u>sistema</u> a E e V constantes, haverá diminuição espontânea do volume de um <u>subsistema</u> cuja pressão é menor que a pressão das suas vizinhanças.

Solução.



$$(1)\quad \begin{cases} V = V_1 + V_2 \rightarrow \text{cte} \\ E = E_1 + E_2 \rightarrow \text{cte} \end{cases}$$

Admita que V_1 possa variar, logo V_2 também! Portanto de (1) $dS_1 + dS_2 > 0$

Para t qualquer $\rightarrow$ $\frac{dS_1}{dt} + \frac{dS_2}{dt} > 0$ (1)

Como $V_1 = V_1(t)$ e $V_2 = V_2(t)$.

$$\left(\frac{\partial S_1}{\partial V_1}\right)\frac{dV_1}{dt} + \left(\frac{\partial S_2}{\partial V_2}\right)\frac{dV_2}{dt} > 0 \quad (\text{regra da cadeia})$$

Além disso $\frac{dV_1}{dt} = -\frac{dV_2}{dt_2}$

$\times$ $dE = TdS - pdV$

$\frac{dS}{dV} = \frac{p}{T}$

Como E é constante

$$\left(\frac{p_1}{T_1}\right)\left(\frac{dV_1}{dt}\right) + \left(\frac{p_2}{T_2}\right)\left(\frac{dV_2}{dt}\right) > 0 \quad (2)$$

continuação

Se o sistema está em equilíbrio térmico

$$T_1 = T_2 = T$$

$\therefore$ de (2) e lembrando que $\dfrac{dV_1}{dt} = -\dfrac{dV_2}{dt}$

Para o subsistema (p_1, V_1)

$$\left(\frac{p_1}{T}\right)\left(\frac{dV_1}{dt}\right) + \left(\frac{p_2}{T}\right)\left(-\frac{dV_1}{dt}\right) > 0$$

$$(p_1)\left(\frac{dV_1}{dt}\right) - (p_2)\frac{dV_1}{dt} > 0$$

Logo $(p_1 - p_2)\left(\dfrac{dV_1}{dt}\right) > 0$. Mas $\dfrac{dV_1}{dt} < 0$

Temos $(p_1 - p_2)(-) > 0$.

Portanto $(p_1) < (p_2)$

O subsistema 1 diminui de volume onde a pressão externa $p_2 > p_1$

Problema 2)

Demonstrar que, sendo Y um parâmetro de energia de um sistema,

$$\left\langle \frac{\partial E}{\partial Y} \right\rangle = (\partial H/\partial Y)_{S,p}.$$

Solução:

Temos

$$dE = TdS - p\,dV + \gamma\,dY$$

$$dH = TdS + V\,dp + \gamma\,dY$$

$$\therefore \quad (dE)_{S,V} = (dH)_{S,p}.$$

$$(dE)_{S,V} = \gamma\,dY \quad ; \quad (dH)_{S,p} = \gamma\,dY$$

$$\therefore \quad \left(\frac{dE}{dY}\right) = \left(\frac{dH}{dY}\right) = \left\langle \left(\frac{\partial E}{\partial Y}\right) \right\rangle = \left(\frac{\partial H}{\partial Y}\right)_{S,p}$$

Obs: $E = E(p, q, Y)$

$$\frac{dE}{dt} = \left(\frac{\partial E}{\partial Y}\right)\frac{\partial Y}{\partial t} \rightarrow \boxed{\frac{dE}{dt} = \left\langle \left(\frac{\partial E}{\partial Y}\right) \right\rangle \cdot \frac{dY}{dt}}$$

$$\frac{dE}{dt} = \left(\frac{\partial E}{\partial Y}\right)_S \frac{dY}{dt} \quad \therefore \quad \left(\frac{\partial E}{\partial Y}\right)_{S,V} = \left\langle \left(\frac{\partial E}{\partial Y}\right) \right\rangle$$

<Sistema mecânico>

Problema 3

Demonstrar que $E = -T^2 \left(\frac{\partial F/T}{\partial T}\right)_V$

Solução:

$F = E - TS \qquad dF = dE - TdS - SdT$

e que $dE = TdS - p\,dV$.

$dF = -S\,dT - p\,dV \Rightarrow \left(\frac{\partial F}{\partial T}\right)_V = -S$

$\therefore \quad S = -\left.\frac{\partial F}{\partial T}\right)_V^{**} \qquad p = -\left.\frac{\partial F}{\partial V}\right)_T$

das eqs. Maxwell

$\left.\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

Como $F = E - TS$ $\quad (**) \Rightarrow E = F + TS$

$E = F - T \left.\frac{\partial F}{\partial T}\right)_V$

$E = -T^2 \left(\frac{\partial F/T}{\partial T}\right)$

Usando a transformada de Legendre para S.

Transformada

$$\Psi(p) = -px + y \rightarrow \begin{cases} p = dy/dx \\ y = f(x) = F(S) \end{cases}$$

$$\Psi(p) = E$$

$$y = F \qquad p = \frac{dF}{dS} = \frac{\partial F}{\partial S}$$

$$\therefore \Psi(p) = -\frac{\partial F}{\partial S} \cdot S + F$$

$$\therefore E = F - \frac{\partial F}{\partial S} \cdot S$$

$$E = -S^2 \left(\frac{\partial F/S}{\partial S} \right)$$

faz $S \rightarrow T$

$$E = -T^2 \left(\frac{\partial F/T}{\partial T} \right)$$

Problema 4)

Seja $S = S(U,V,N)$, obtenha a função de Massieu. $J = S - U/T$.

Solução

Como $S = S(U,V,N)$

$$dS = \frac{\partial S}{\partial U}.dU + \frac{\partial S}{\partial V}.dV + \frac{\partial S}{\partial N}.dN \quad (1)$$

Mas $dU = TdS - p\,dV + \mu dN$

$$\therefore\ dS = \left(\frac{dU}{T}\right) + \frac{p}{T}dV - \mu\frac{dN}{T} \quad (2)$$

Como $\dfrac{dU}{T} = d(U/T) - U\,d(1/T)$

de (2) $\quad dS = d(U/T) - U(d(1/T) + \dfrac{p}{V}dV - \mu dN$

Logo $\quad d(S - U/T) = -U(d(1/T)) + \dfrac{p}{T}dV - \mu dN$

$$\Downarrow$$

$$dJ = -U\,d(1/T) + \frac{p}{T}dV - \mu dN \quad (3)$$

$\therefore\ J = S - U/T$

como $J = J(1/T, V, N)$

$$dJ = \frac{\partial J}{\partial(1/T)} d(1/T) + \frac{\partial J}{\partial V} dV + \frac{\partial J}{\partial N} dN \quad (4)$$

como de (3) $dJ = -U\,d(1/T) + \frac{p}{T} dV - \mu dN$

Temos

$$\frac{\partial J}{\partial(1/T)} = -U$$

$$\frac{\partial J}{\partial V} = \frac{p}{T} \quad \text{e} \quad \frac{\partial J}{\partial N} = -\mu$$

Obs: pela transformada de Legendre

$S(U,V)$	$J = J(1/T, V)$
$1/T = (\partial S/\partial U)_V$	$-U = \partial J/\partial(1/T)$
$J = S - U/T$	$S = U/T + J$
eliminando S e U $J = J(1/T, V)$	eliminando $1/T$ e J $S = S(U,V)$

E1-2

Substituímos S(T, V, N) na relação F = U – TS, e obtemos:

$$F(T,V,N) = \frac{3}{2}NkT - NkT\left[s_0 + \ln\left\{\left(\frac{3}{2}\frac{NkT}{U_0}\right)^{3/2}\left(\frac{N_0}{N}\right)^{5/2}\left(\frac{V}{V_0}\right)\right\}\right]$$

Usando a relação $U_0 = 3/2\ N_0\ k\ T_0$ obtemos:

$$F(T,V,N) = NkT\left[\frac{3}{2} - s_0 - \ln\left\{\left(\frac{T}{T_0}\right)^{3/2}\left(\frac{N_0}{N}\right)\left(\frac{V}{V_0}\right)\right\}\right]$$

A partir de F, obtemos facilmente:

$$S(T,V,N) = -\left.\frac{\partial F}{\partial T}\right|_{V,N} = Nk\left[s_0 + \ln\left\{\left(\frac{T}{T_0}\right)^{3/2}\left(\frac{N_0}{N}\right)\left(\frac{V}{V_0}\right)\right\}\right]$$

$$p(T,V,N) = -\left.\frac{\partial F}{\partial V}\right|_{T,N} = \frac{NkT}{V}$$

$$\mu(T,V,N) = \left.\frac{\partial F}{\partial N}\right|_{T,V} = kT\left[\frac{5}{2} - s_0 - \ln\left\{\left(\frac{T}{T_0}\right)^{3/2}\left(\frac{N_0}{N}\right)\left(\frac{V}{V_0}\right)\right\}\right]$$

A partir das expressões anteriores podemos escrever U(T, V, N):

$$U(T,V,N) = F(T,V,N) + TS = \frac{3}{2}NkT$$

E1-1

Exemplo 1: energia livre de Helmholtz do gás ideal

A equação fundamental U = U(S, V, N) para um gás ideal pode ser escrita na forma:

$$U(S,V,N) = U_0 \left(\frac{N}{N_0}\right)^{5/3} \left(\frac{V_0}{V}\right)^{2/3} \exp\left\{\frac{2}{3}\left(\frac{S}{Nk} - s_0\right)\right\}$$

Calcule a energia livre de Helmholtz, e determine a partir dela a entropia S(T,V,N), a pressão p(T,V, N) e o potencial químico μ(T,V,N).

SOLUÇÃO:

Devemos substituir S por T na expressão: F = U – TS.

Para isso, obtemos T:

$$T = \left.\frac{\partial U}{\partial S}\right|_{N,V,\ldots} = U_0 \left(\frac{N}{N_0}\right)^{5/3} \left(\frac{V_0}{V}\right)^{2/3} \times \exp\left\{\frac{2}{3}\left(\frac{S}{Nk} - s_0\right)\right\} \frac{2}{3Nk}$$

Invertendo esta expressão, temos:

$$S(T,V,N) = Nk\left[s_0 + \ln\left\{\left(\frac{3}{2}\frac{NkT}{U_0}\right)^{3/2} \left(\frac{N_0}{N}\right)^{5/2} \left(\frac{V}{V_0}\right)\right\}\right]$$

E2-1

Exemplo 2: entalpia do gás ideal

Calcule a entalpia de um gás ideal a partir da equação fundamental:

$$U(S, V, N) = U_0 \left(\frac{N}{N_0}\right)^{5/3} \left(\frac{V_0}{V}\right)^{2/3} \exp\left\{\frac{2}{3}\left(\frac{S}{Nk} - s_0\right)\right\}$$

SOLUÇÃO:

Devemos substituir V por p na expressão: H = U + p V.

Primeiro obtemos p(S, V, N):

$$-p = \left.\frac{\partial U}{\partial V}\right|_{S,N,\ldots} = -\frac{2}{3} U_0 \left(\frac{N}{N_0}\right)^{5/3} \frac{V_0^{2/3}}{V^{5/3}} \exp\left\{\frac{2}{3}\left(\frac{S}{Nk} - s_0\right)\right\}$$

Invertendo a última expressão, temos:

$$\frac{V}{V_0} = \left(\frac{2}{3}\frac{U_0}{pV_0}\right)^{3/5} \left(\frac{N}{N_0}\right) \exp\left\{\frac{2}{5}\left(\frac{S}{Nk} - s_0\right)\right\}$$

Substituindo em H = U + p V:

$$H(S, p, N) = U_0 \left(\frac{N}{N_0}\right) \left(\frac{2}{3}\frac{U_0}{pV_0}\right)^{-2/5} \exp\left\{\frac{2}{5}\left(\frac{S}{Nk} - s_0\right)\right\}$$
$$+ pV_0 \left(\frac{2}{3}\frac{U_0}{pV_0}\right)^{3/5} \left(\frac{N}{N_0}\right) \exp\left\{\frac{2}{5}\left(\frac{S}{Nk} - s_0\right)\right\}$$

Combinando ambos termos, temos:

$$H(S, p, N) = \frac{5}{3} U_0 \left(\frac{N}{N_0}\right) \left(\frac{2}{3}\frac{U_0}{pV_0}\right)^{-2/5} \exp\left\{\frac{2}{5}\left(\frac{S}{Nk} - s_0\right)\right\}$$

Usando $U_0 = 3/2\ N_0 k T_0 = 3/2\ p_0 V_0$ temos:

$$H(S, p, N) = \frac{5}{3} U_0 \left(\frac{N}{N_0}\right) \left(\frac{2}{3}\frac{U_0}{pV_0}\right)^{-2/5} \exp\left\{\frac{2}{5}\left(\frac{S}{Nk} - s_0\right)\right\}$$

As equações de estado são:

$$T(S,p,N) = \left.\frac{\partial H}{\partial S}\right|_{p,N}$$

$$= \frac{2U_0}{3N_0k}\left(\frac{p}{p_0}\right)^{2/5}\exp\left\{\frac{2}{5}\left(\frac{S}{Nk}-s_0\right)\right\}$$

$$V(S,p,N) = \left.\frac{\partial H}{\partial p}\right|_{S,N}$$

$$= \frac{2U_0}{3p_0}\left(\frac{N}{N_0}\right)\left(\frac{p}{p_0}\right)^{-3/5}\exp\left\{\frac{2}{5}\left(\frac{S}{Nk}-s_0\right)\right\}$$

$$\mu = \left.\frac{\partial H}{\partial N}\right|_{S,p} = \frac{5U_0}{3N_0}\left(1-\frac{2S}{5Nk}\right)\left(\frac{p}{p_0}\right)^{2/5}\exp\left\{\frac{2}{5}\left(\frac{S}{Nk}-s_0\right)\right\}$$

Obs: verifique que

$$U = H - pV = \frac{3}{2}NkT \;!!$$