Universidade de São Paulo
Instituto de Química

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Cálculo de funções termodinâmicas em diferentes temperaturas

Primeira lei e entalpia

$$\left.\begin{aligned} dU &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \\ dH &= \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \end{aligned}\right\} dn = 0$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

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

Como calcular H para qualquer T?

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \Rightarrow \int_{T_1}^{T_2} dH = \int_{T_1}^{T_2} C_P dT$$

Se não ocorre transição de fase:

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_P dT$$

$$\Downarrow$$

$$\Delta H(T_2) = \Delta H(T_1) + \int_{T_1}^{T_2} \Delta C_P dT$$

Lei de Kirchhoff

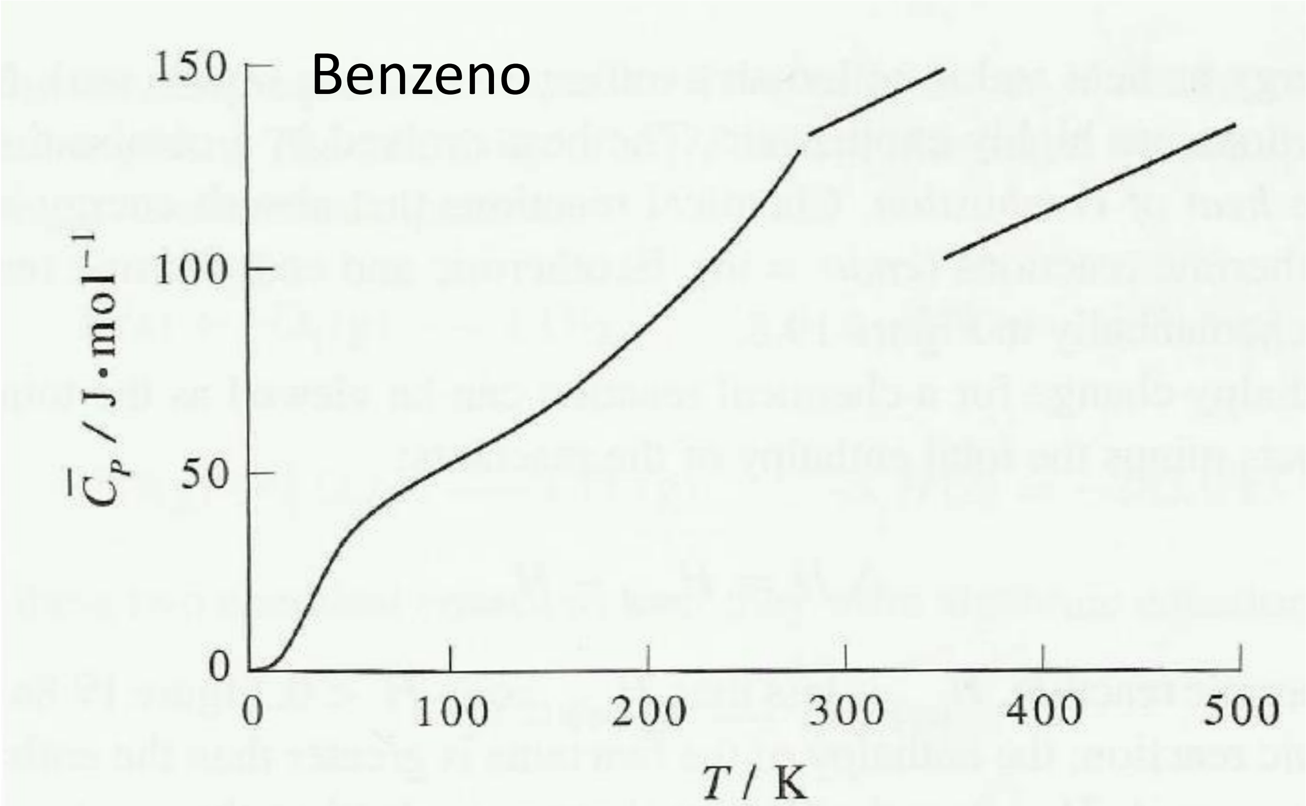
Lei de Kirchhoff

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_P \, dT \qquad \Delta H(T_2) = \Delta H(T_1) + \int_{T_1}^{T_2} \Delta C_P \, dT$$

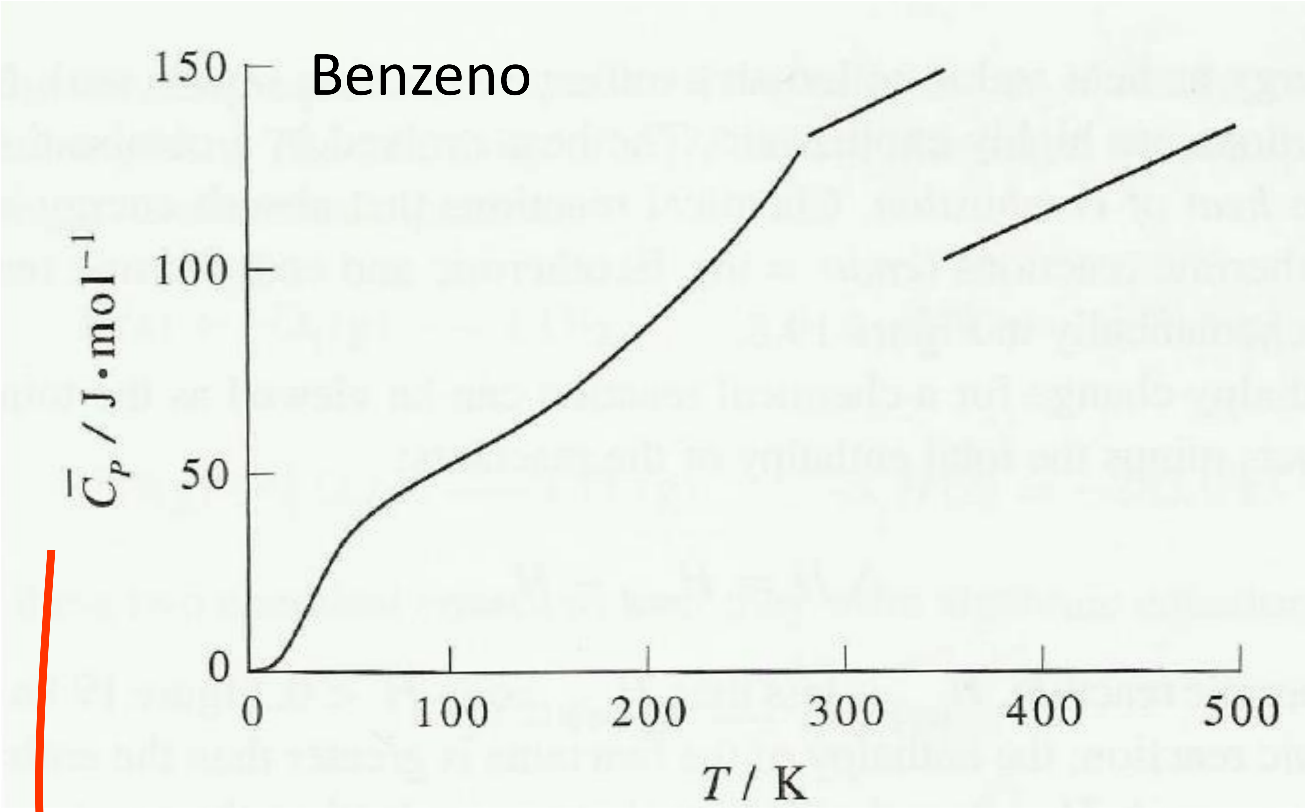
Se $\dfrac{dC_P}{dt} = 0$

$$H(T_2) = H(T_1) + C_P \Delta T \qquad \Delta H(T_2) = \Delta H(T_1) + \Delta C_P \Delta T$$

Comportamento de $C_p(T)$



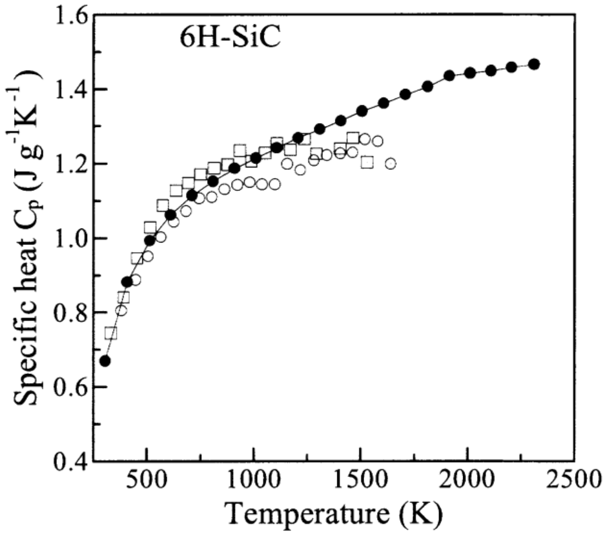
Comportamento de $C_p(T)$



Expandir $C_p(T)$ em série?

$$\Delta Cp = \Delta a + \Delta bT + \Delta cT^2 + \Delta dT^3$$

Expansão em série de C_P



$$C_p \quad = a + bT + cT^2 + dT^3$$

$$\Delta Cp \quad = \Delta a + \Delta bT + \Delta cT^2 + \Delta dT^3$$

Substance	a J K^{-1} mol^{-1}	b 10^{-2} J K^{-2} mol^{-1}	c 10^{-5} J K^{-3} mol^{-1}	d 10^{-9} J K^{-4} mol^{-1}
N_2 (g)	28.883	-0.157	0.808	-2.871
O_2 (g)	25.460	1.519	-0.715	1.311
H_2 (g)	29.088	-0.192	0.400	-0.870
CO (g)	28.142	0.167	0.537	-2.221
CO_2 (g)	22.243	5.977	-3.499	7.464
H_2O (g)	32.218	0.192	1.055	-3.593
NH_3 (g)	24.619	3.75	-0.138	–
CH_4 (g)	19.875	5.021	1.268	-11.004

Nilsson, O., H. Mehling, R. Horn, J. Fricke, R. Hofmann, S.G. Muller, R. Eckstein, D. Hofmann, *High Temperatures-High Pressures* **29** (1997), 73-79.

Para qualquer ΔT

$$\Delta H(T_2) = \Delta H(T_1) + \int_{T_1}^{T_{trans_1}} \Delta C_{P_1} dT + \Delta Htrans_1 + \int_{T_{trans_1}}^{T_2} \Delta C_{P_2} dT + \ \ldots$$

$$\Delta Cp \ \ = \Delta a + \Delta bT + \Delta cT^2 + \Delta dT^3$$

Se não ocorre transição de fase:

$$\Delta\Delta H = \int_{T_1}^{T_2} \Delta a + \Delta bT + \Delta cT^2 \ + \Delta dT^3 \ dT$$

$$\Delta\Delta H(T_2) = \Delta a \Delta T + \frac{1}{2} \Delta b \Delta T^2 + \frac{1}{3} \Delta c \Delta T^3 \ + \frac{1}{4} \Delta d \Delta T^4$$

Primeira lei e entalpia

$$\left.\begin{aligned} dU &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \\ dH &= \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \end{aligned}\right\} dn = 0$$

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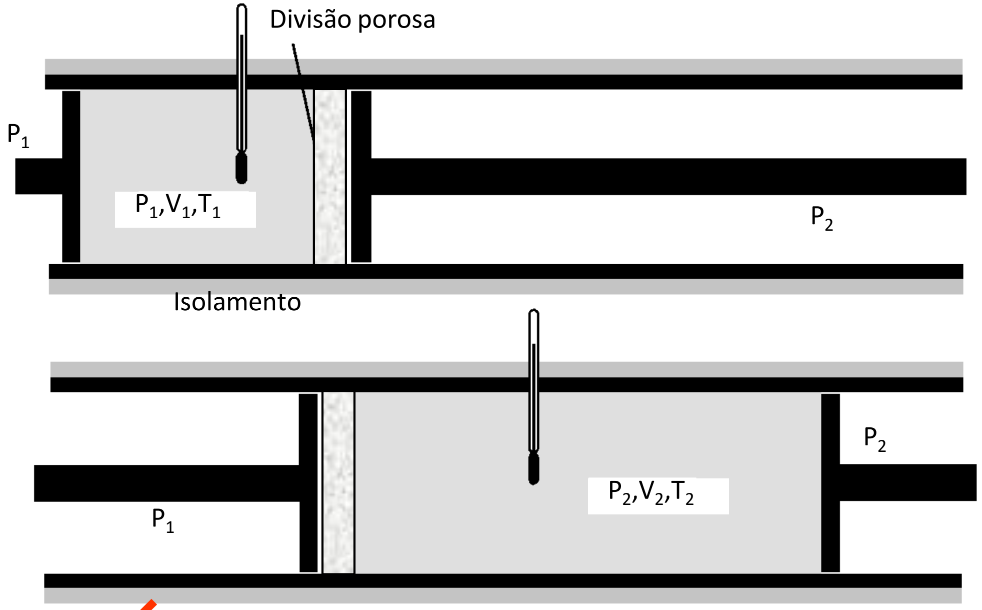
$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_U = -C_V\,\mu_J$$

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H = -C_P\,\mu_{JT}$$

Experimento de Joule-Thomson



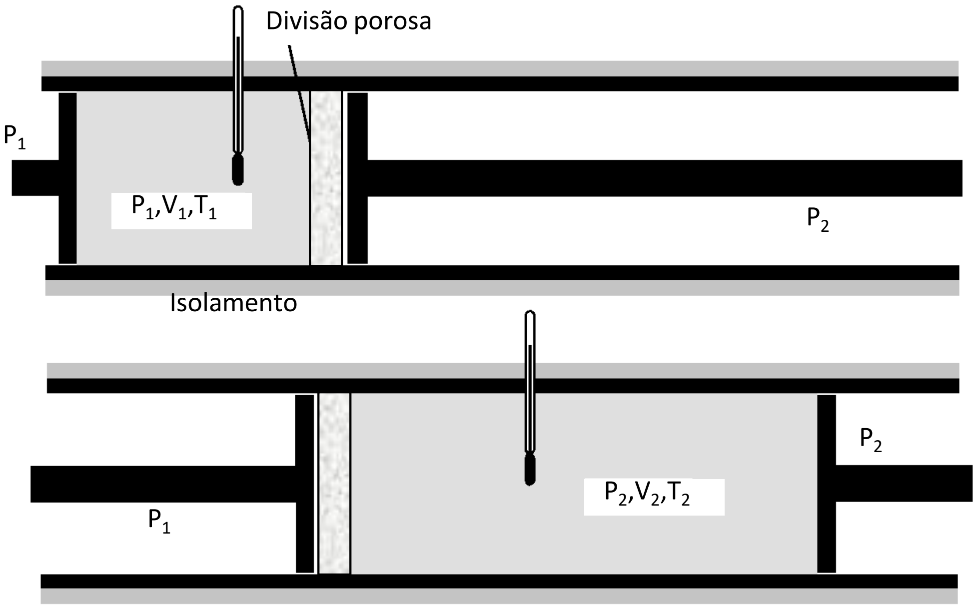
adiabático $q = 0$

Velocidade do êmbolo pode ser controlada para manter $dP_1 = dP_2 = 0$ e $P_2 < P_1$

$$\Delta U = \int_1^2 dU = U_2 - U_1 = \int_1^2 (dq + dw)$$

$$\Delta U = w_{total} = w_1 + w_2$$

Processo isoentálpico



$$w_1 = -\int_{V_1}^{0} PdV = -P_1 \int_{V_1}^{0} dV = P_1V_1$$

$$w_2 = -\int_{0}^{V_2} PdV = -P_2 \int_{0}^{V_2} dV = -P_2V_2$$

$$U_2 - U_1 = w_1 + w_2 \Rightarrow U_2 - U_1 = P_1V_1 - P_2V_2$$

$$U_1 + P_1V_1 = U_2 + P_2V_2$$

$$\boxed{H_1 = H_2} \Rightarrow dH = 0$$

Coeficiente de Joule-Thomson

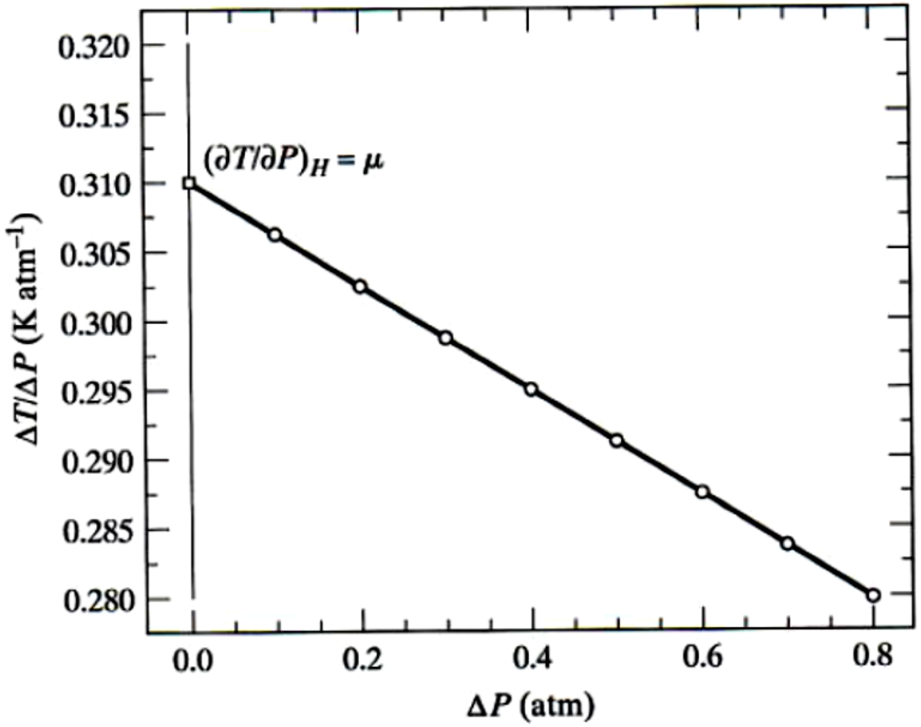
$$dH = C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \qquad dH = 0$$

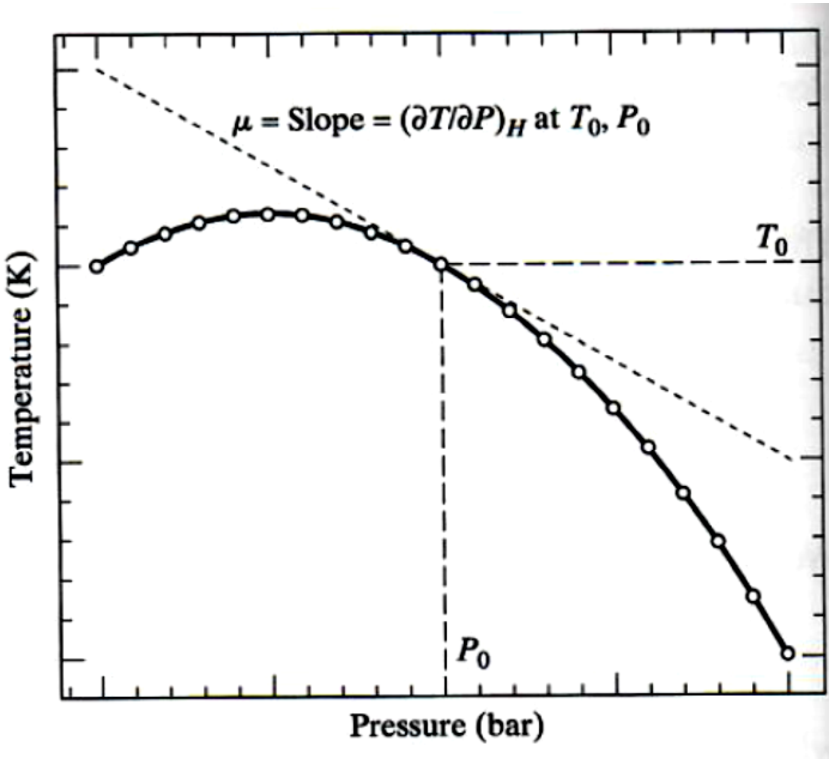
$$\left(\frac{\partial H}{\partial P}\right)_T dP = -C_P dT \qquad \left(\frac{\partial H}{\partial P}\right)_T = -C_p \underbrace{\left(\frac{\partial T}{\partial P}\right)_H}_{\mu_{JT}}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = -C_p\, \mu_{JT}$$

$$\left(\frac{\partial T}{\partial P}\right)_H = \lim_{\Delta P \to 0} \left(\frac{\Delta T}{\Delta P}\right)_H$$

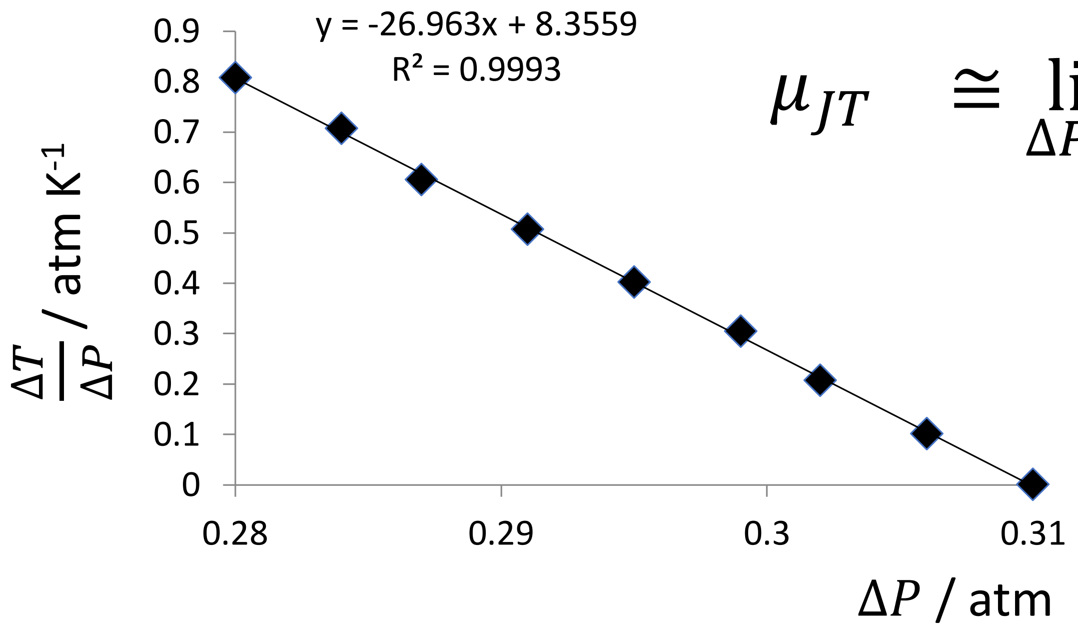
Resultados experimentais



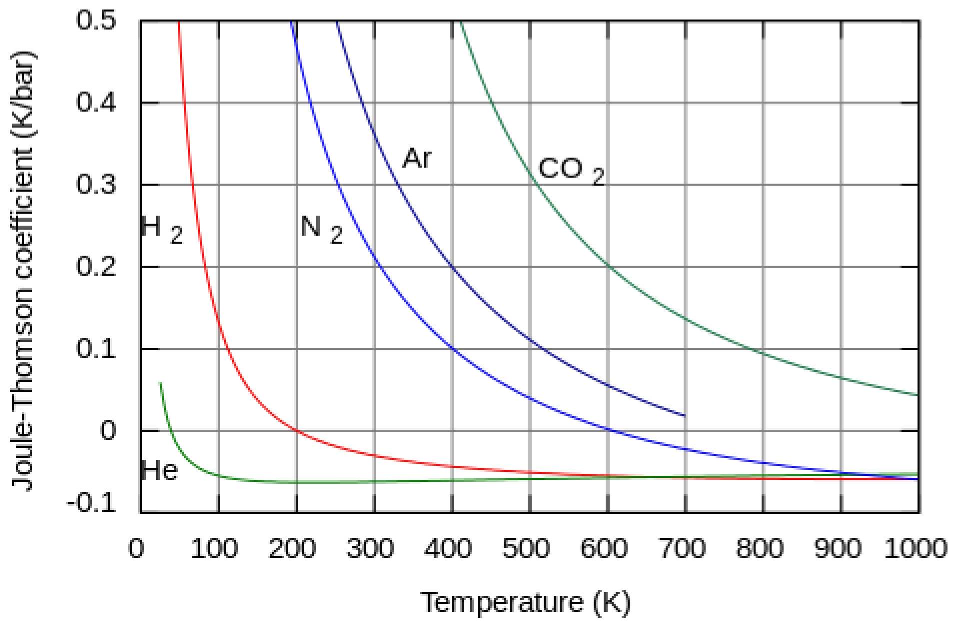


$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = \lim_{\Delta P \to 0} \left(\frac{\Delta T}{\Delta P}\right)_H$$

Coeficiente de Joule-Thomson



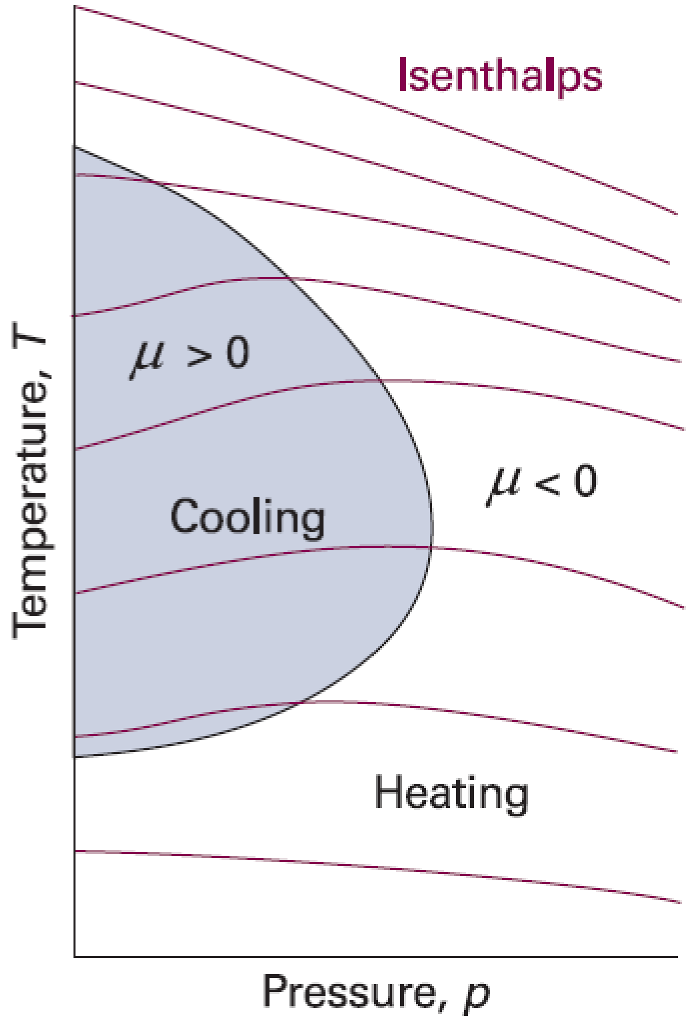
$$\mu_{JT} \cong \lim_{\Delta P \to 0} \left(\frac{\Delta T}{\Delta P} \right)_H$$

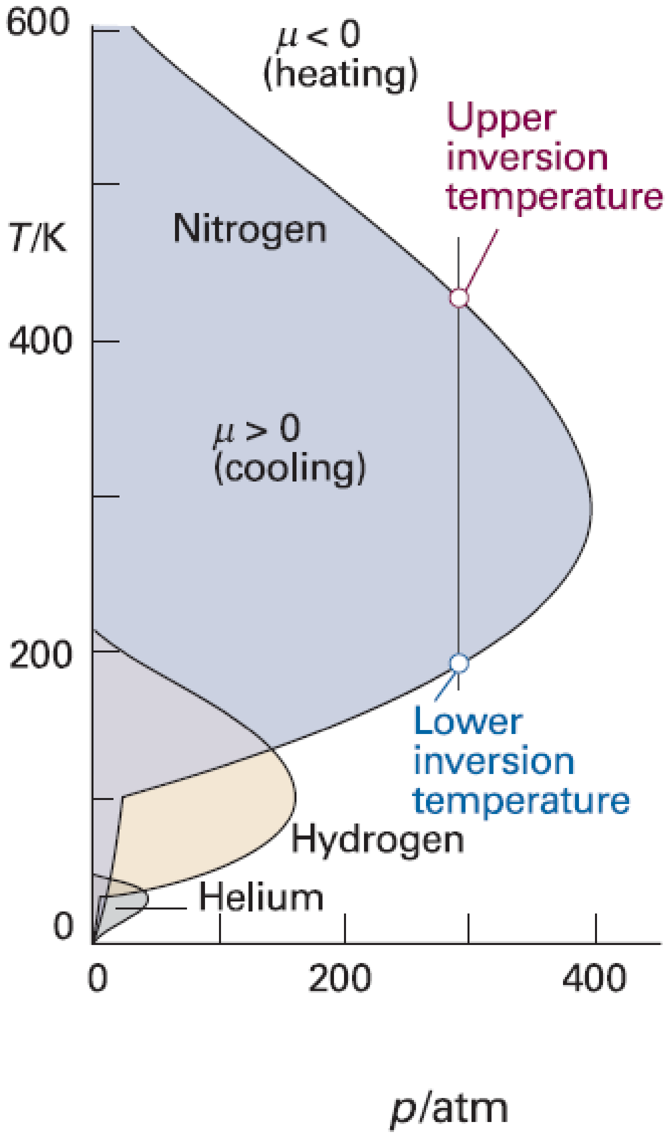


Derivada total: $$dH = \underbrace{C_P}\, dT - \underbrace{\mu_{JT}\, C_p}\, dP$$

taxas de variação

Expansão de gás





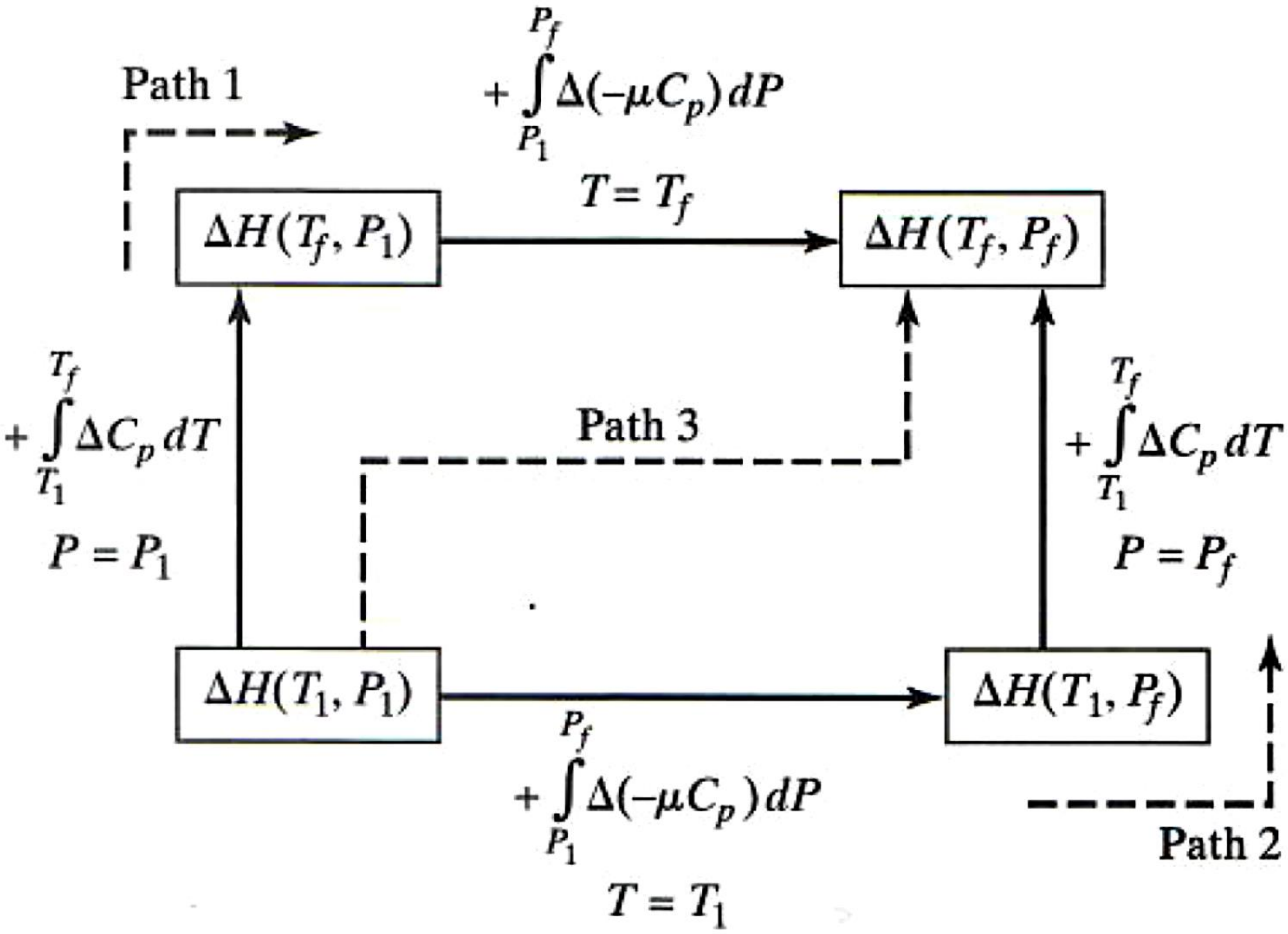
$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$$

Alguns exemplos

Menino maluquinho: panela de pressão fica presa na cabeça de menino de 3 anos em SE

http://www.mundowalmart.com.br/wp-content/uploads/2011/11/05_alimentacao_panela.jpg
https://br.noticias.yahoo.com/blogs/vi-na-internet/menino-maluquinho-panela-press%C3%A3o-fica-presa-na-cabe%C3%A7a-191018262.html

Finalmente!


Path 1
$+\int_{P_1}^{P_f} \Delta(-\mu C_p)\, dP$
$T = T_f$
$\Delta H(T_f, P_1)$
$\Delta H(T_f, P_f)$
$+\int_{T_1}^{T_f} \Delta C_p\, dT$
$P = P_1$
Path 3
$+\int_{T_1}^{T_f} \Delta C_p\, dT$
$P = P_f$
$\Delta H(T_1, P_1)$
$\Delta H(T_1, P_f)$
$+\int_{P_1}^{P_f} \Delta(-\mu C_p)\, dP$
$T = T_1$
Path 2

Primeira lei e entalpia

$$\left.\begin{aligned} dU &= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \\ dH &= \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \end{aligned}\right\} dn = 0$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P \quad \mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad \mu_J = \left(\frac{\partial T}{\partial V}\right)_U$$

$$\left.\begin{aligned} dH &= C_P dT - \mu_{JT} C_p dP \\ dU &= C_V dT - \mu_J C_V dV \end{aligned}\right\} dn = 0$$