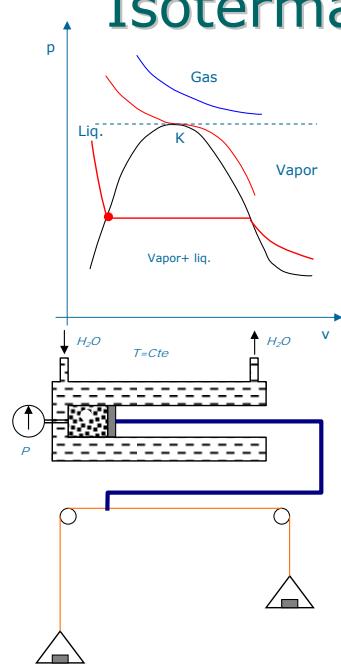




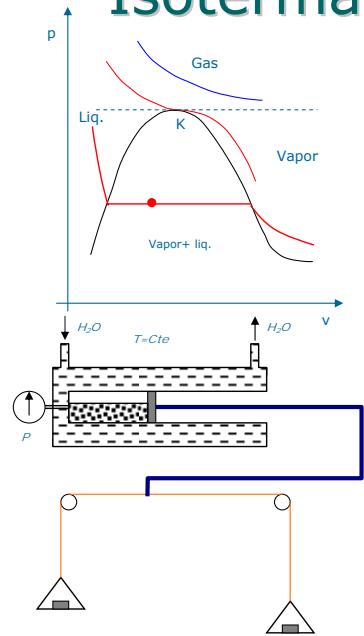
Vapores y gases reales



Isotermas de Andrew



Isotermas de Andrew



Isotermas de Andrew

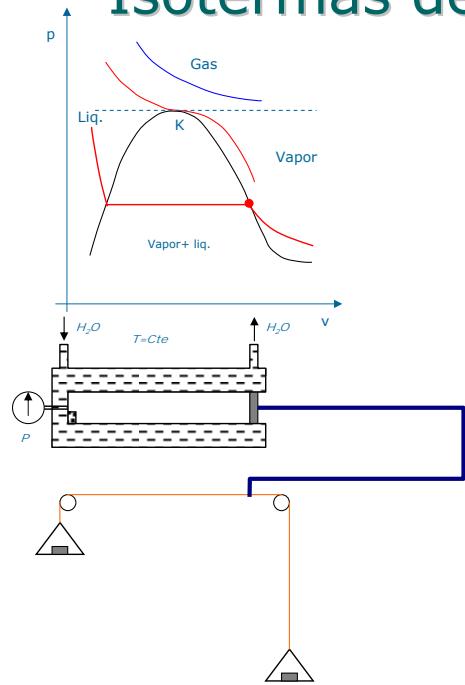
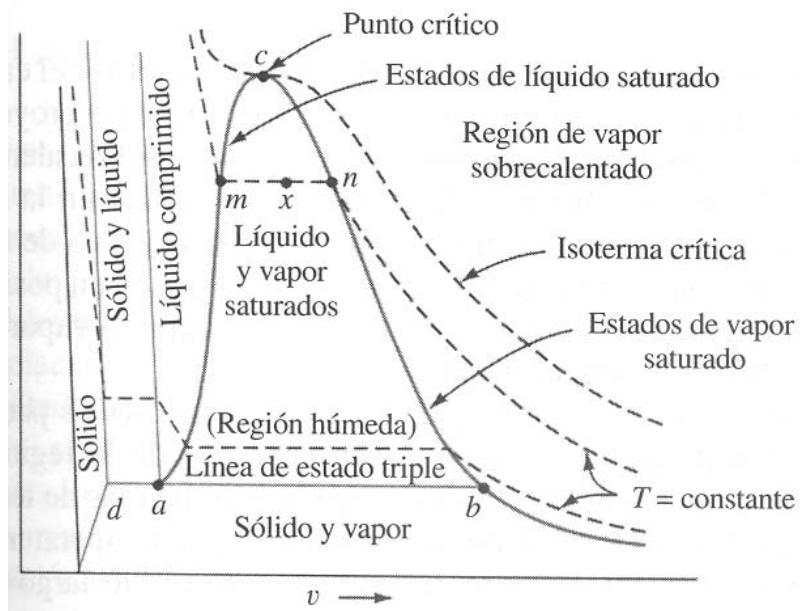
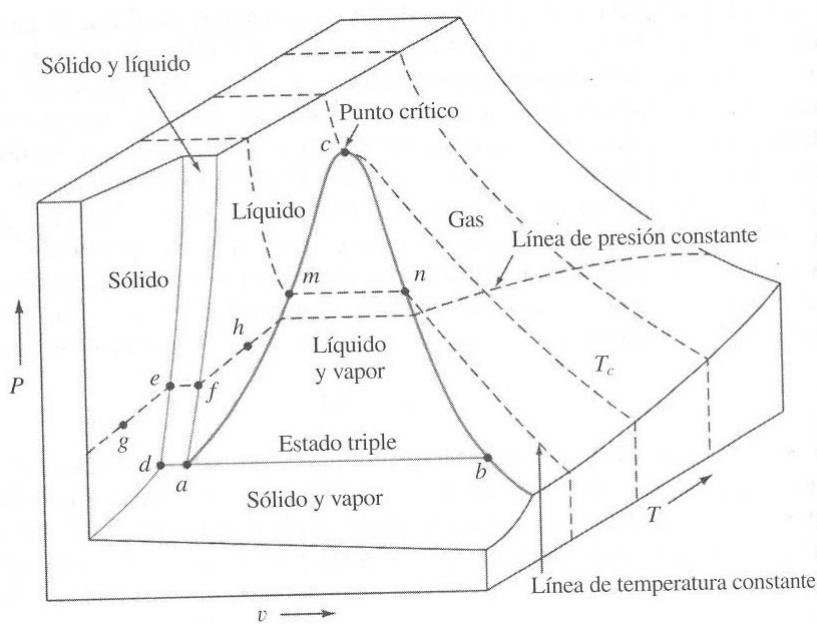


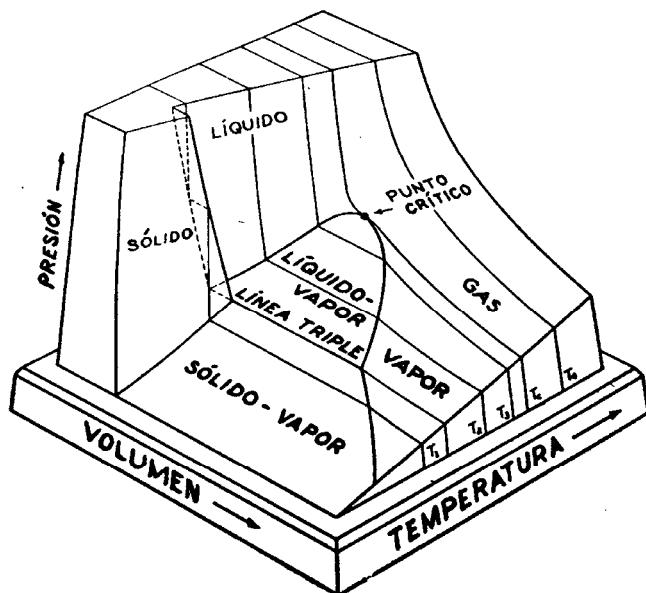
Diagrama p,v de una sustancia pura



Superficie p,v,T de una sustancia pura



Superficie p,v,T de una sustancia pura



Regla de las Fases



Función de Gibbs

$$G = H - T \cdot S$$

$$dG = dH - T \cdot dS - S \cdot dT$$

Si la transformación es reversible

$$dH = T \cdot dS + V \cdot dp$$

$$dG = T \cdot dS + V \cdot dp - T \cdot dS - S \cdot dT$$

$$dG = V \cdot dp - S \cdot dT$$

Si $dp=0$ y $dT=0$

$$dG_{pT} = 0$$

$$G1 = G2$$

Regla de las fases

$$T = cte$$

$$P = cte$$

$$G_1 = m_L \cdot g_L + m_v \cdot g_v$$

$$G_2 = (m_L - dm_v) \cdot g_L + (m_v + dm_v) \cdot g_v$$

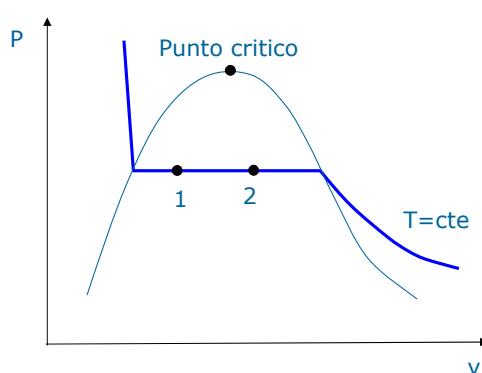
$$G_2 = m_L \cdot g_L + m_v \cdot g_v + dm_v(g_v - g_L)$$

$$G_2 = G_1 + dm_v(g_v - g_L)$$

$$dG_{pT} = 0$$

$$G1 = G2$$

$$g_v = g_L$$



Generalizando: p/ F fases

$$g^i = g^{ii} = g^{iii} = \dots = g^F$$

Regla de las fases

Nº de grados de libertad

$$v = a - b$$

a: Nº de variables

b= Nº de ecuaciones

Nº de variables

Nº de variables por fase = (C-1)químicos + 2 físicos

$$a = (C - 1)F + 2F = (C + 1)F$$

C: Nº de componentes

F: Nº de fases

Nº de ecuaciones

$$\begin{aligned} C_1 & \left\{ \begin{array}{l} F_1 \rightarrow g_1^i \\ F_2 \rightarrow g_1^{ii} \\ F_3 \rightarrow g_1^{iii} \\ \vdots \\ F_F \rightarrow g_1^F \end{array} \right. \\ C & \left\{ \begin{array}{l} g_1^i = g_1^{ii} = g_1^{iii} = \dots = g_1^F \\ g_2^i = g_2^{ii} = g_2^{iii} = \dots = g_2^F \\ g_C^i = g_C^{ii} = g_C^{iii} = \dots = g_C^F \\ p^i = p^{ii} = p^{iii} = \dots = p^F \\ T^i = T^{ii} = T^{iii} = \dots = T^F \end{array} \right. \end{aligned}$$

$(F-1)C$
 $b = (F-1)C + (F-1)2$
 $b = (F-1).(C+2)$
 $(F-1)2$

Regla de las fases

Nº de grados de libertad

$$v = a - b$$

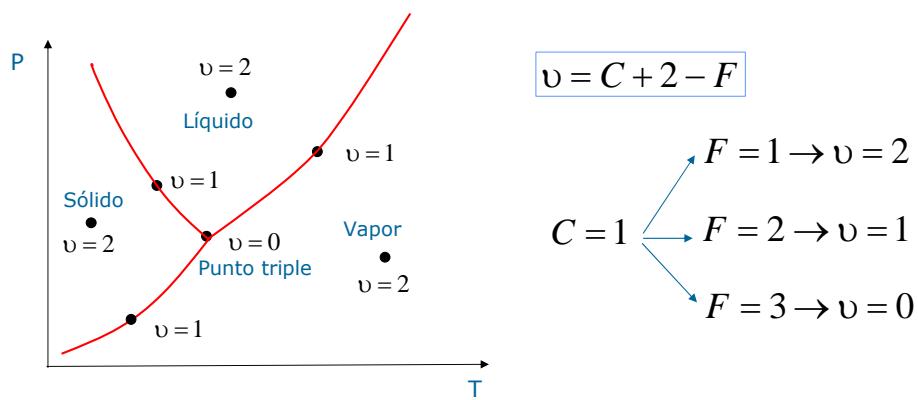
$$a = (C - 1)F + 2F = (C + 1)F$$

$$b = (F - 1).(C + 2)$$

$$v = \cancel{(CF + F)} - \cancel{(CF - C + 2F - 2)}$$

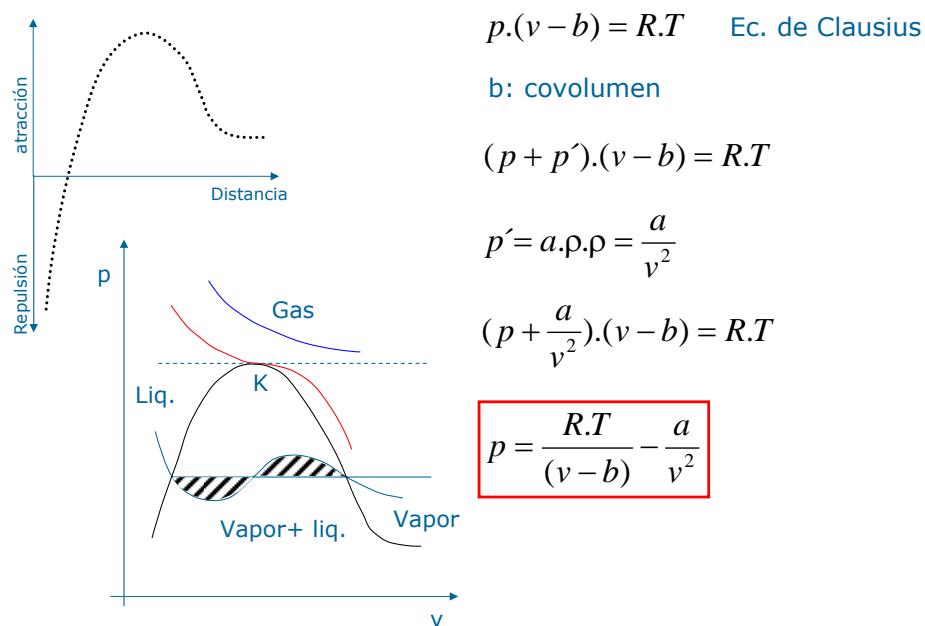
$$v = C + 2 - F$$

Regla de las fases: sustancia pura

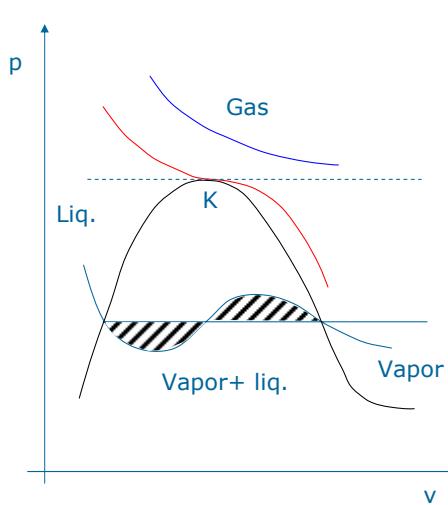




Gases Reales



Gases Reales, Van Der Waals



$$p_c = \frac{RT_c}{v_c - b} - \frac{a}{v_c^2}$$

$$\left(\frac{\delta p}{\delta v} \right)_T = -\frac{R.T_c}{(v_c - b)^2} + \frac{2.a}{v_c^3} = 0$$

$$\frac{R.T_c}{(v_c - b)^2} = \frac{2.a}{v_c^3}$$

Eliminando R.T_c

$$\frac{p_c + \frac{a}{v_c^2}}{v_c - b} = \frac{2.a}{v_c^3}$$

$$\frac{p_c + \frac{a}{v_c^2}}{(v_c - b).2.a} = \frac{1}{v_c^3}$$

Ec. A

Van Der Waals

$$\left(\frac{\delta^2 p}{\delta v^2} \right)_T = \frac{2.R.T_c}{(v_c - b)^3} - \frac{6.a}{v_c^4} = 0$$

$$\frac{2.R.T_c}{(v_c - b)^3} = \frac{6.a}{v_c^4}$$

$$\frac{R.T_c}{v_c - b} = p_c + \frac{a}{v_c^2}$$

Mult. x 2 y dividiendo por (vc-b)²

$$\frac{2.R.T_c}{(v_c - b)^3} = \frac{2 \left(p_c + \frac{a}{v_c^2} \right)}{(v_c - b)^2}$$

$$\frac{6.a}{v_c^4} = \frac{2 \left(p_c + \frac{a}{v_c^2} \right)}{(v_c - b)^2}$$

$$\frac{3(v_c - b)}{2.v_c^4} = \frac{p_c + \frac{a}{v_c^2}}{2.a.(v_c - b)}$$

$$\frac{p_c + \frac{a}{v_c^2}}{(v_c - b).2.a} = \frac{1}{v_c^3}$$

Ec. A

$$\frac{3(v_c - b)}{2.v_c^4} = \frac{1}{v_c^3}$$

Van Der Waals

$$\frac{3(v_c - b)}{2.v_c^4} = \frac{1}{v_c^3}$$

$$3(v_c - b) = 2.v_c$$

$$b = \frac{v_c}{3}$$

$$\frac{p_c + \frac{a}{v_c^2}}{(v_c - b).2.a} = \frac{1}{v_c^3}$$

$$\frac{p_c + \frac{a}{v_c^2}}{(v_c - \frac{v_c}{3}).2.a} = \frac{1}{v_c^3}$$

Ec. A

$$p_c + \frac{a}{v_c^2} = \frac{4.a}{3.v_c^2}$$

$$p_c = \frac{a}{3.v_c^2}$$

$$a = 3.p_c.v_c^2$$

$$p_c = \frac{RT_c}{v_c - b} - \frac{a}{v_c^2}$$

$$p_c = \frac{RT_c}{\frac{2.v_c}{3}} - \frac{3.p_c.v_c^2}{v_c^2}$$

$$R = \frac{8}{3} \cdot \frac{p_c \cdot v_c}{T_c}$$

Estados correspondientes

$$\left(p + \frac{a}{v^2} \right) \cdot (v - b) = R.T$$

$$a = 3.p_c.v_c^2$$

$$b = \frac{v_c}{3}$$

Reemplazando a y b

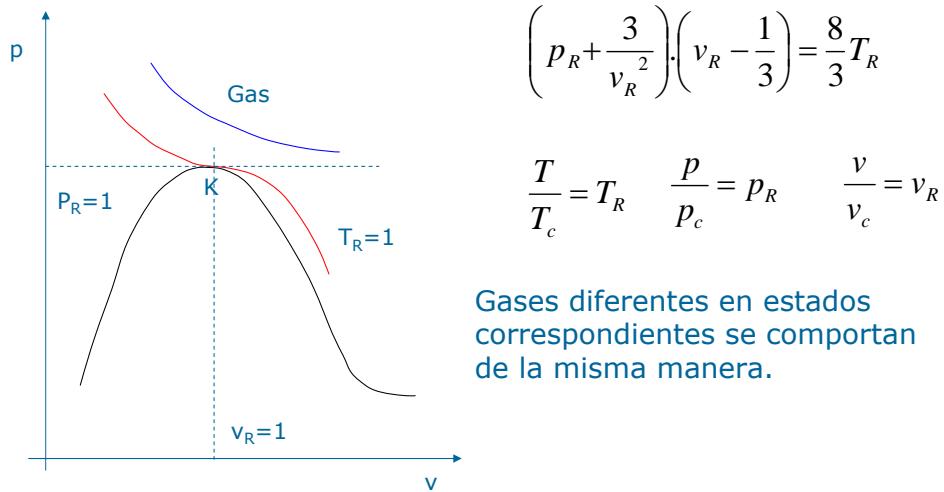
$$\left(p + \frac{3.p_c.v_c^2}{v^2} \right) \cdot \left(v - \frac{v_c}{3} \right) = \frac{8}{3} \frac{p_c \cdot v_c}{T_c} \cdot T$$

$$\left(\frac{p}{p_c} + \frac{3}{\left(\frac{v}{v_c} \right)^2} \right) \cdot \left(\frac{v}{v_c} - \frac{1}{3} \right) = \frac{8}{3} \frac{T}{T_c}$$

$$\frac{T}{T_c} = T_R \quad \frac{p}{p_c} = p_R \quad \frac{v}{v_c} = v_R$$

$$\left(p_R + \frac{3}{v_R^2} \right) \cdot \left(v_R - \frac{1}{3} \right) = \frac{8}{3} T_R$$

Estados correspondientes



Coeficiente de compresibilidad

$$p.v = Z.R.T$$

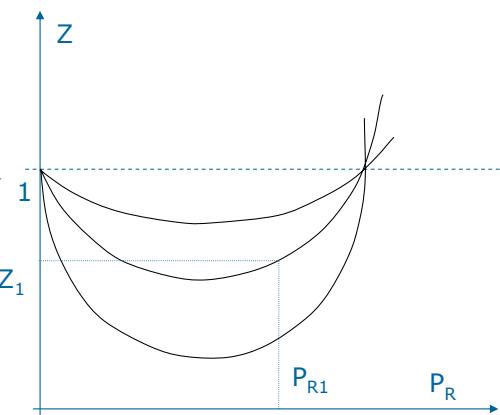
$$Z = f(p, T)$$

$$v_{real} = \frac{Z.R.T}{p} \quad v_{ideal} = \frac{R.T}{p}$$

$$v_{real} - v_{ideal} = \frac{R.T}{p} \cdot (Z - 1)$$

$$\frac{T}{T_c} = T_R \quad \frac{p}{p_c} = p_R$$

$$Z = f_2(p_R, T_R)$$



Coeficiente de compresibilidad

Analizando 2 gases diferentes en estados correspondientes.

$$T_{R1} = T_{R2} \quad p_{R1} = p_{R2}$$

$$z_1 = z_2 \quad v_{R1} \neq v_{R2}$$

$$Z = \frac{p \cdot v}{R \cdot T} \quad \frac{p_1 \cdot v_1}{R_1 \cdot T_1} = \frac{p_2 \cdot v_2}{R_2 \cdot T_2}$$

$$p_1 = p_{R1} \cdot p_{c1} \quad T_1 = T_{R1} \cdot T_{c1}$$

$$p_2 = p_{R2} \cdot p_{c2} \quad T_2 = T_{R2} \cdot T_{c2}$$

$$\frac{p_{c1} \cdot p_{R1} \cdot v_1}{R_1 \cdot T_{C1} \cdot T_{R1}} = \frac{p_{c2} \cdot p_{R2} \cdot v_2}{R_2 \cdot T_{C2} \cdot T_{R2}}$$

$$\frac{v_1}{R_1 \cdot T_{C1}} = \frac{v_2}{R_2 \cdot T_{C2}}$$

Vol. Crítico ideal o pseudocrítico

$$v_{ci1} = \frac{R_1 \cdot T_{c1}}{p_{c1}} \quad v_{ci2} = \frac{R_2 \cdot T_{c2}}{p_{c2}}$$

Vol. reducido ideal o pseudoreducido

$$v_{Ri1} = \frac{v_1}{v_{ci1}} \quad v_{Ri2} = \frac{v_2}{v_{ci2}}$$

Gases diferentes en estados correspondientes tienen volúmenes pseudoreducidos iguales.

$$v_{Ri1} = v_{Ri2}$$

Ec. De Beattie-Bridgman

$$p = \frac{R \cdot T \cdot \left(1 - \frac{c}{v \cdot T^3}\right)}{v^2} \cdot \left(v + Bo \left(1 - \frac{b}{v}\right)\right) - \frac{Ao}{v^2} \cdot \left(1 - \frac{a}{v}\right)$$

- 1928
- 5 ctes tabuladas para diferentes substancias.
- válida para densidades de hasta el 80% de la critica.

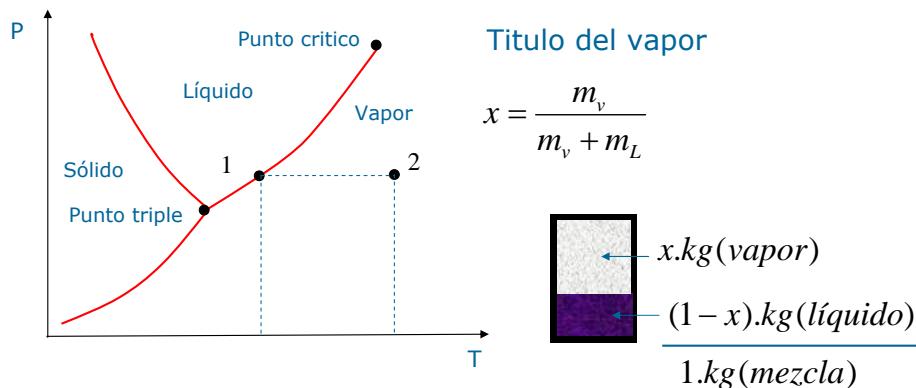


Vapores: definiciones

Vapor saturado: vapor en equilibrio con su líquido.

Líquido saturado: líquido en equilibrio con su vapor.

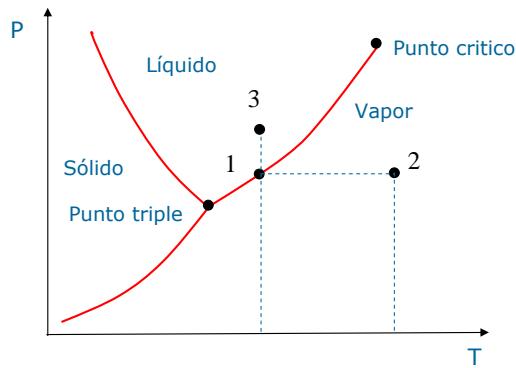
Vapor húmedo: mezcla de vapor saturado y líquido saturado.



Vapores: definiciones

Vapor sobrecalentado: vapor a una temperatura superior a la del equilibrio con su líquido (2).

Líquido comprimido: líquido sometido a una presión mayor que la presión de equilibrio correspondiente a su temperatura (3).



Parámetros extensivos

$$\text{Volumen específico} \quad v = x.v^{ii} + (1-x).v^i$$

$$v = x.v^{ii} + v^i - x.v^i$$

$$v = x(v^{ii} - v^i) + v^i$$

$$x = \frac{v - v^i}{v^{ii} - v^i}$$

$$\text{Entalpía específica} \quad h = x.h^{ii} + (1-x).h^i \quad x = \frac{h - h^i}{h^{ii} - h^i}$$

$$\text{Entropía específica} \quad s = x.s^{ii} + (1-x).s^i \quad x = \frac{s - s^i}{s^{ii} - s^i}$$

Entalpía de vaporización

Diferencia de entalpías entre el vapor saturado y el líquido saturado.

$$r = h^{ii} - h^i$$

$$r = u^{ii} - u^i + p.(v^{ii} - v^i)$$

$$g^{ii} = g^i$$

$$g^{ii} + dg^{ii} = g^i + dg^i$$

$$dg^{ii} = dg^i$$

$$dg = v.dp - s.dT$$

$$v^i.dp - s^i.dT = v^{ii}.dp - s^{ii}.dT$$

$$(s^{ii} - s^i).dT = (v^{ii} - v^i).dp$$

$$(s^{ii} - s^i) = \frac{r}{T}$$

$$\frac{r}{T}dT = (v^{ii} - v^i).dp$$

$$r = T.(v^{ii} - v^i).\frac{dp}{dT}$$

Ecuación de Clapeyron-Clausius.

Ecuación aproximada para calcular presiones de vapor

Hipótesis simplificativas:

- $V^i \ll V^{ii} \rightarrow V^i \approx 0$
- El vapor saturado es un gas perfecto
- $r = r_0 = \text{cte}$ en un entorno

$$r = T.(v^{ii} - v^i).\frac{dp}{dT}$$

$$\frac{r_0.dT}{R.T^2} = \frac{dp}{p}$$

$$\ln \frac{p}{p_0} = \frac{r_0}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)$$

Valida para bajas presiones.

$$v^{ii} = \frac{R.T}{p}$$

$$r_0 = \frac{R.T^2}{p} \cdot \frac{dp}{dT}$$

Diagrama entrópicos para vapores

$$s = f(T, p)$$

$$ds = \left(\frac{\partial s}{\partial T} \right)_p dT + \left(\frac{\partial s}{\partial p} \right)_T dp$$

$$ds = \frac{\delta Q_R}{T}$$

$$\delta Q_R = dh - v.dp$$

$$ds = \frac{1}{T} dh - \frac{v}{T} dp$$

$$h = f(T, p)$$

$$dh = \left(\frac{\partial h}{\partial T} \right)_p dT + \left(\frac{\partial h}{\partial p} \right)_T dp$$

$$ds = \frac{1}{T} \left(\frac{\partial h}{\partial T} \right)_p dT + \frac{1}{T} \left[\left(\frac{\partial h}{\partial p} \right)_T - v \right] dp$$

$$\left(\frac{\partial s}{\partial T} \right)_p = \frac{1}{T} \left(\frac{\partial h}{\partial T} \right)_p$$

$$\left(\frac{\partial h}{\partial T} \right)_p = c_p$$

$$\left(\frac{\partial s}{\partial T} \right)_p = \frac{c_p}{T}$$

Diagrama entrópicos para vapores

$$ds = \left(\frac{\partial s}{\partial T} \right)_p dT + \left(\frac{\partial s}{\partial p} \right)_T dp \quad ds = \frac{1}{T} \left(\frac{\partial h}{\partial T} \right)_p dT + \frac{1}{T} \left[\left(\frac{\partial h}{\partial p} \right)_T - v \right] dp$$

$$\left(\frac{\partial s}{\partial T} \right)_p = \frac{1}{T} \left(\frac{\partial h}{\partial T} \right)_p$$

$$\boxed{\left(\frac{\partial s}{\partial p} \right)_T = \frac{1}{T} \left[\left(\frac{\partial h}{\partial p} \right)_T - v \right]}$$

$$\left(\frac{\partial^2 s}{\partial T \partial p} \right) = \left(\frac{\partial^2 s}{\partial p \partial T} \right)$$

$$\frac{1}{T} \left(\frac{\partial^2 h}{\partial T \partial p} \right) = \frac{-1}{T^2} \cdot \left[\left(\frac{\partial h}{\partial p} \right)_T - v \right] + \frac{1}{T} \cdot \left[\left(\frac{\partial^2 h}{\partial p \partial T} \right) - \left(\frac{\partial v}{\partial T} \right)_p \right] =$$

$$= \frac{-1}{T^2} \left(\frac{\partial h}{\partial p} \right)_T - \frac{-1}{T^2} \cdot v + \frac{1}{T} \left(\frac{\partial^2 h}{\partial p \partial T} \right) - \frac{1}{T} \cdot \left(\frac{\partial v}{\partial T} \right)_p$$

Diagrama entrópicos para vapores

$$\cancel{\frac{1}{T} \cdot \left(\frac{\partial^2 h}{\partial T \partial p} \right)} = \frac{-1}{T^2} \cdot \left(\frac{\partial h}{\partial p} \right)_T - \frac{-1}{T^2} \cdot v + \frac{1}{T} \cdot \cancel{\left(\frac{\partial^2 h}{\partial p \partial T} \right)} - \frac{1}{T} \cdot \left(\frac{\partial v}{\partial T} \right)_p \quad \left(\frac{\partial^2 h}{\partial T \partial p} \right) = \left(\frac{\partial^2 h}{\partial p \partial T} \right)$$

$$\left(\frac{\partial h}{\partial p} \right)_T = v - T \left(\frac{\partial v}{\partial T} \right)_p \quad \boxed{\left(\frac{\partial s}{\partial p} \right)_T = \frac{1}{T} \left[\left(\frac{\partial h}{\partial p} \right)_T - v \right]}$$

$$\left(\frac{\partial s}{\partial p} \right)_T = - \left(\frac{\partial v}{\partial T} \right)_p$$

$$ds = \left(\frac{\partial s}{\partial T} \right)_p dT + \left(\frac{\partial s}{\partial p} \right)_T dp$$

$$ds = c_p \cdot \frac{dT}{T} - \left(\frac{\partial v}{\partial T} \right)_p dp$$

Diagrama entrópicos para vapores

$$ds = c_p \cdot \frac{dT}{T} - \left(\frac{\partial v}{\partial T} \right)_p dp$$

Para estados alejados del P_c

$$c_p \cdot \ln \frac{T_2}{T_1} \gg v_0 \cdot \int_{p_1}^{p_2} \alpha \cdot dp$$

$$\alpha = \frac{1}{v_0} \cdot \left(\frac{\partial v}{\partial T} \right)_p$$

$$s_2 - s_1 = c_p \cdot \ln \frac{T_2}{T_1}$$

$$\left(\frac{\partial v}{\partial T} \right)_p = v_0 \cdot \alpha$$

Adopt. S₀=0 p/líquido a T₀=273K

$$ds = c_p \cdot \frac{dT}{T} - \alpha \cdot v_0 \cdot dp$$

$$s = c_p \cdot \ln \frac{T}{T_0}$$

$$s_2 - s_1 = c_p \cdot \ln \frac{T_2}{T_1} - v_0 \cdot \int_{p_1}^{p_2} \alpha \cdot dp$$

$$T = T_0 \cdot e^{\frac{s}{c_p}}$$

Variación del C_p con T

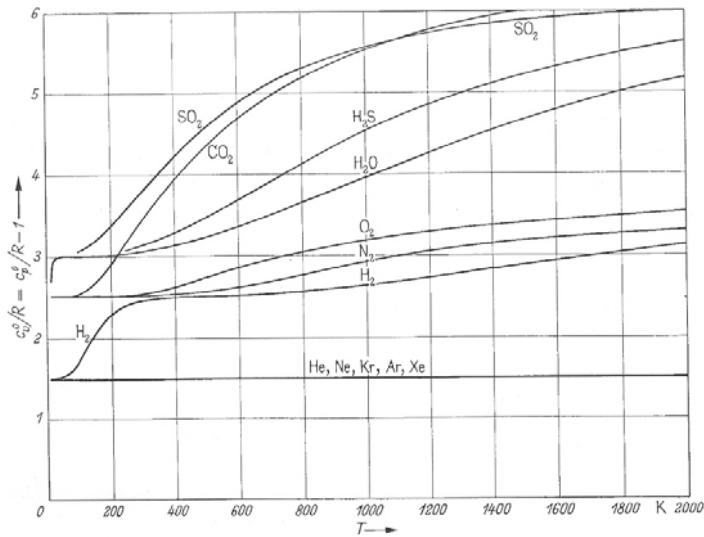


Diagrama entrópicos para vapores

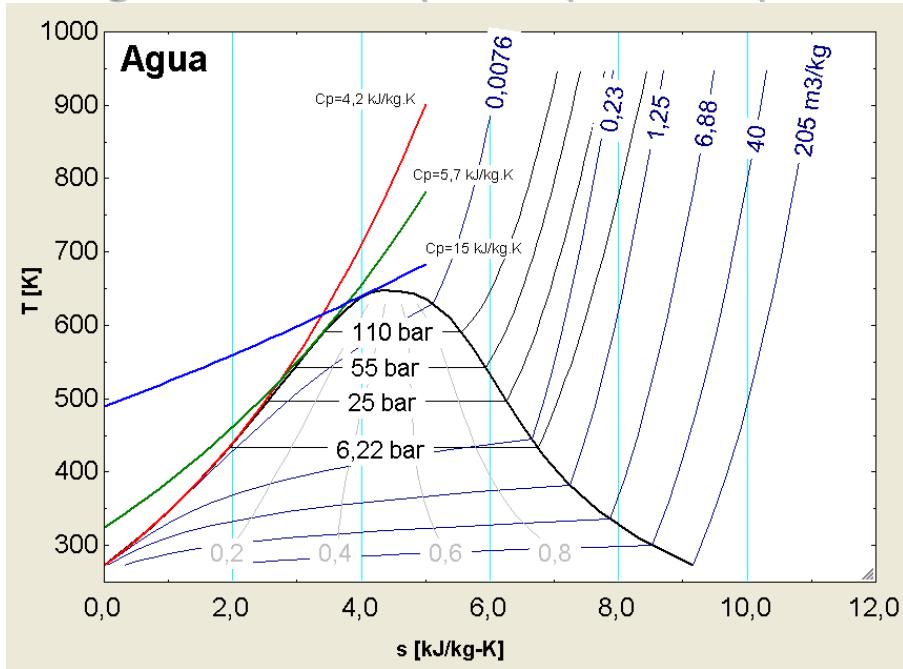


Diagrama entrópicos para vapores

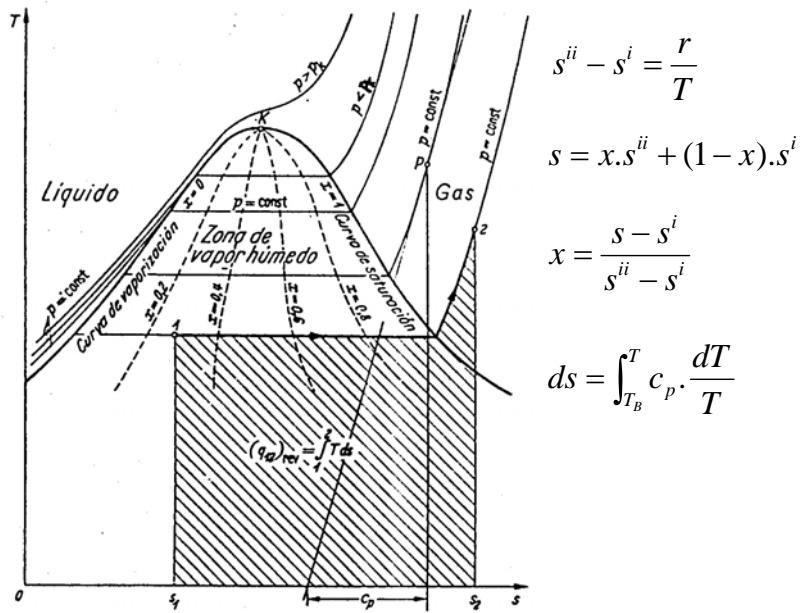


Diagrama entrópico para agua

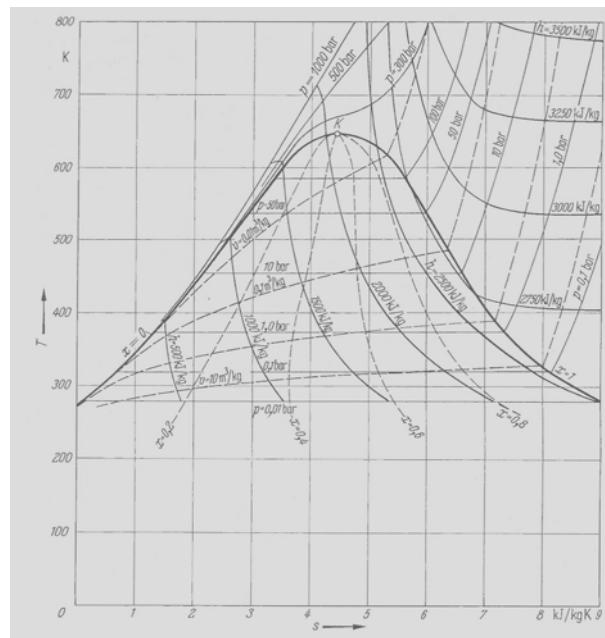
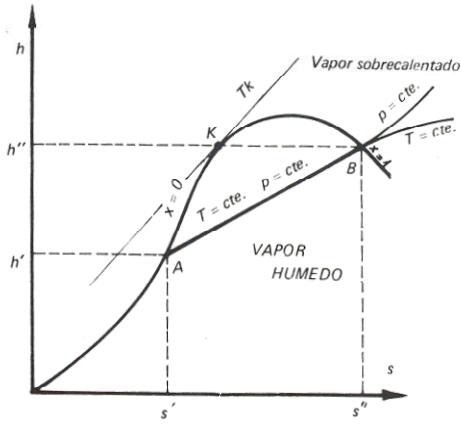


Diagrama de Mollier



$$dh = c_p \cdot dT + \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] dp$$

Para agua líquida

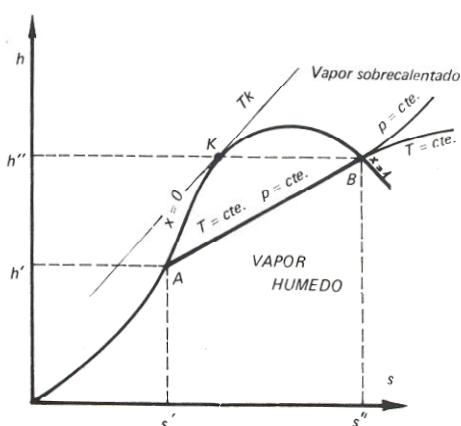
$$dh = c_p \cdot dT$$

$$h_2 - h_1 = c_p \cdot (T_2 - T_1)$$

Adopt. $h_0=0$ $p/T_0=273K$

$$\dot{h} = c_p \cdot (T - T_0) = c_p \cdot t$$

Diagrama de Mollier



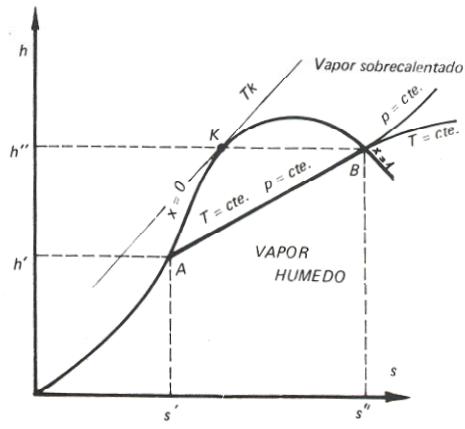
Curva límite superior

$$h'' = h' + r$$

$$s'' = s' + \frac{r}{T}$$

$$\frac{h'' - h'}{s'' - s'} = \frac{r}{T} = T$$

Diagrama de Mollier



Pendiente de las isobáricas

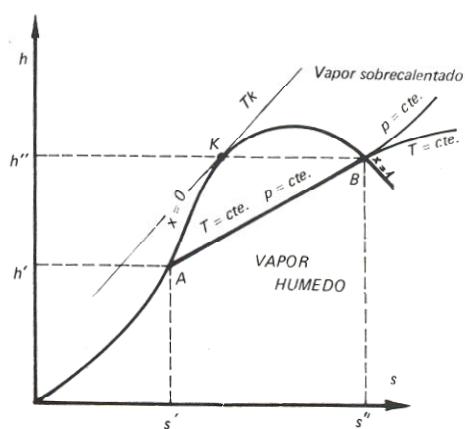
$$\left(\frac{\partial h}{\partial s}\right)_p = \frac{\left(\frac{\partial h}{\partial T}\right)_p}{\left(\frac{\partial s}{\partial T}\right)_p} = \frac{c_p}{\left(\frac{\partial v}{\partial T}\right)_p} = T$$

Pendiente de una isotérmica

$$\left(\frac{\partial h}{\partial s}\right)_T = \frac{\left(\frac{\partial h}{\partial p}\right)_T}{\left(\frac{\partial s}{\partial p}\right)_T} = \frac{v - T \cdot \left(\frac{\partial v}{\partial T}\right)_P}{-\left(\frac{\partial v}{\partial T}\right)_P}$$

$$\left(\frac{\partial h}{\partial s}\right)_T = T - v \cdot \left(\frac{\partial T}{\partial v}\right)_p$$

Diagrama de Mollier



Zona heterogénea

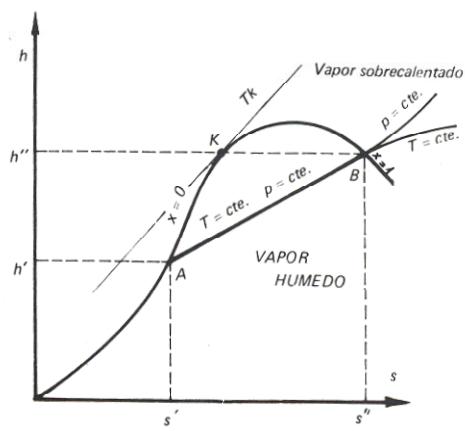
$$\left(\frac{\partial T}{\partial v}\right)_p = 0$$

$$\left(\frac{\partial h}{\partial s}\right)_T = T = \left(\frac{\partial h}{\partial s}\right)_p$$

Zona vapor sobrecalentado

$$\left(\frac{\partial h}{\partial s}\right)_T \rightarrow 0$$

Diagrama de Mollier



Si el gas se comporta como gas perfecto $h=f(T)$ y si $T=cte$ y $h=cte$

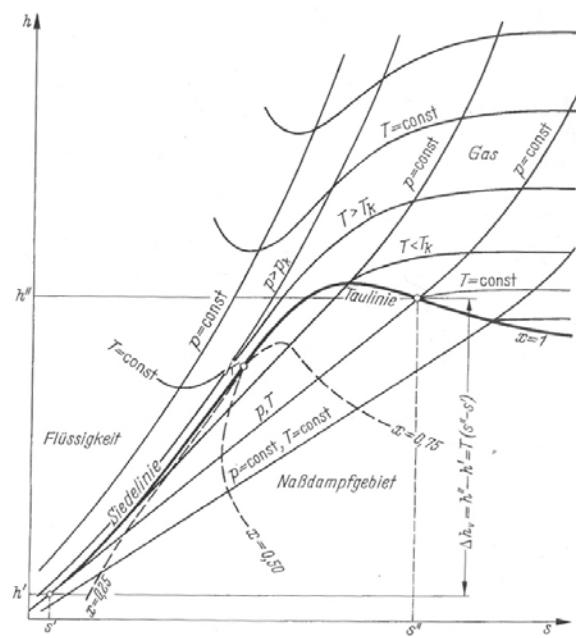
$$T = \frac{p \cdot v}{R}$$

$$\left(\frac{\partial T}{\partial v} \right)_p = \frac{p}{R}$$

$$\left(\frac{\partial h}{\partial s} \right)_T = T - v \cdot \left(\frac{\partial T}{\partial v} \right)_p$$

$$\left(\frac{\partial h}{\partial s} \right)_T = T - v \cdot \frac{p}{R} = T - T = 0$$

Diagrama de Mollier





Mezclas de gases perfectos

Características de la composición

$$m = \sum m_i$$

$$g_i = \frac{m_i}{m} \quad \text{Fracción en masa}$$

$$\sum g_i = 1$$

Fracción molar

$$x_i = \frac{n_i}{n}$$

$$n_A = \frac{m_A}{M_A}$$

$$n = \sum n_i \quad n = \frac{m_A}{M_A} + \frac{m_B}{M_B} + \dots$$

Masa molar de la mezcla

$$M_m = \frac{m}{n} \quad M_m = \sum x_i \cdot M_i$$

Conversión entre másica y molar

$$x_A = \frac{n_A}{n} = \frac{m_A}{M_A} \cdot \frac{M_m}{m} = g_A \cdot \frac{M_m}{M_A}$$

$$g_A = x_A \cdot \frac{M_A}{M_m}$$

$$n = n_A + n_B + \dots$$

$$\frac{m}{M_m} = \frac{m_A}{M_A} + \frac{m_B}{M_B} + \dots$$

$$\frac{1}{M_m} = \frac{g_A}{M_A} + \frac{g_B}{M_B} + \dots$$

Mezclas de gases perfectos

Presión parcial

$$p_i = x_i \cdot p$$

$$\sum_{i=1}^n p_i = \sum_{i=1}^n x_i \cdot p = p$$

Ley de Dalton

$$p = n \cdot \frac{R \cdot T}{V} = \left(\sum_{i=1}^n n_i \right) \cdot \frac{R \cdot T}{V}$$

$$p = n_A \cdot \frac{R \cdot T}{V} + n_B \cdot \frac{R \cdot T}{V} + n_C \cdot \frac{R \cdot T}{V} + \dots$$

$$n_A \cdot \frac{R \cdot T}{V} = n_A \cdot \frac{p}{n} = x_A \cdot p = p_A$$

$$p = p_A + p_B + p_C + \dots$$

La presión total es igual a la suma de las presiones que ejercería cada uno de los gases ocupando el volumen total a la misma temperatura.

Ecuación de estado

En magnitudes molares

$$p_A \cdot V = n_A \cdot R \cdot T$$

$$p_B \cdot V = n_B \cdot R \cdot T$$

$$\dots = \dots$$

$$\underline{p \cdot V = n \cdot R \cdot T}$$

En magnitudes específicas

$$p_A \cdot V = m_A \cdot R p_A \cdot T$$

$$p_B \cdot V = m_B \cdot R p_B \cdot T$$

$$\dots = \dots$$

$$\underline{p \cdot V = (m_A \cdot R p_A + m_B \cdot R p_B + \dots) \cdot T = m \cdot R p_m \cdot T}$$

$$R p_m = \Sigma g_i \cdot R p_i$$

$$n \cdot R = m \cdot R p_m$$

$$R p_m = \frac{n}{m} \cdot R$$

$$R p_m = \frac{R}{M_m}$$

Energía interna

En magnitudes molares

$$U = U_A + \dots$$

$$U = n \cdot \bar{u}_m = n_A \cdot \bar{u}_A + n_B \cdot \bar{u}_B$$

$$\bar{u}_m = \sum x_i \cdot \bar{u}_i$$

$$\bar{u}_m = \frac{m}{n} \cdot u_m = M_m \cdot u_m$$

En magnitudes específicas

$$U = U_A + U_B + \dots$$

$$U = m \cdot u_m = m_A \cdot u_A + m_B \cdot u_B + \dots$$

$$u_m = \sum g_i \cdot u_i$$

Calores molares o específicos

En magnitudes molares

$$\bar{c}_v_m = \frac{du_m}{dt}$$

$$\bar{c}_v_m = \sum x_i \cdot \bar{c}_v_i$$

En magnitudes específicas

$$c_v_m = \sum g_i \cdot c_v_i$$

Exponente adiabático

$$\gamma_m = \frac{x_A \cdot c_p A + x_B \cdot c_p B}{x_A \cdot c_v A + \dots}$$

$$\gamma_m \neq \sum x_i \cdot \gamma_i$$