Termodinàmica Fonamental

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planta 11 Despatx 11.61

1.- Tema 1

2.- Tema 2

3.- Tema 3

4.- Tema 4

1.- Tema 1

2.- Tema 2

3.- Tema 3

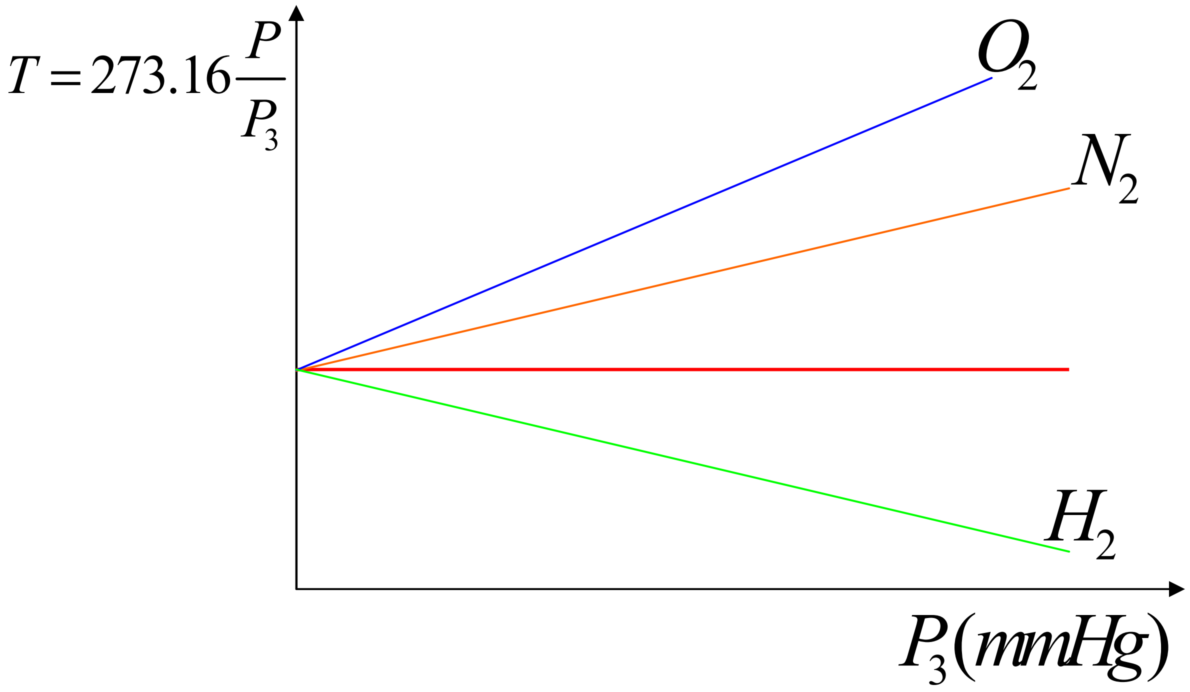
4.- Tema 4

- 2 punts fixes, fusió (t_f) i ebullició de l'aigua (t_v)a 1 atm
- i decidim que t_v-t_f=100 (escala centígrada)

$$t = 100\,\frac{x - x_h}{x_v - x_h}$$

- Determinar la propietat termomètrica a 0 a 100 i a t

2,4,5



$$T = 273.16.\lim_{P_3 \to 0} \frac{P}{P_3}$$

6,7

$$dV(P,T) = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT$$

$$\chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$dV = \alpha V dT - \chi_T V dP$$

$$\frac{dV}{V} = d\ln V = \alpha dT - \chi_T dP$$

$$\boxed{V = V_0 \cdot \exp\left[\alpha \Delta T - \chi_T \Delta P\right]}$$

si α i χ son constants

$$\boxed{V = V_0 \cdot \left[1 + \alpha \Delta T - \chi_T \Delta P\right]}$$

si α i χ son petits

$$S = S_0 \cdot \left[1 + \sigma \Delta T\right] \qquad \sigma = 2\lambda \qquad L = L_0 \cdot \left[1 + \lambda \Delta T\right] \qquad \alpha = 3\lambda$$

Termòmetres	$$t = 100\frac{x - x_h}{x_v - x_h}$$	
Termòmetre g.i.	$$T = 273.16.\lim_{P_3 \to 0}\frac{P}{P_3}$$	
Canvi de volum coefs tèrmics	$$V = V_0 \cdot \exp\left[\alpha\Delta T - \chi_T\Delta P\right]$$ $$V = V_0 \cdot \left[1 + \alpha\Delta T - \chi_T\Delta P\right]$$	

1.- Tema 1

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4.- Tema 4

$$PV = nRT \Leftrightarrow Pv = RT$$

Processos

P=ct (Gay-Loussac)	T=ct (Boyle)	V=ct	n=ct
$\frac{V}{T} = \frac{nR}{P} = ct$	$PV = nRT = ct$	$\frac{P}{T} = \frac{nR}{V} = ct$	$\frac{PV}{T} = nR = ct$

Coeficients tèrmics

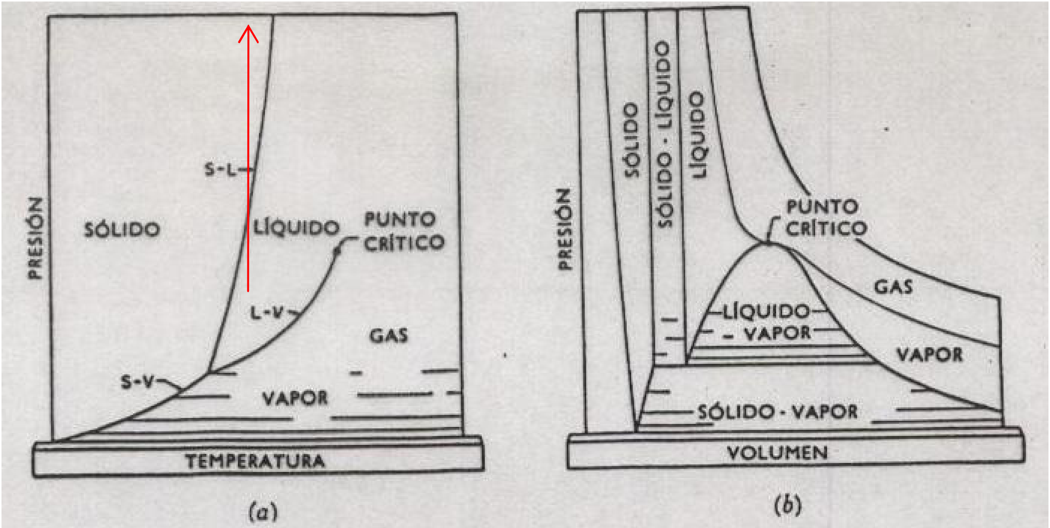
$$\alpha = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = \frac{1}{v}\frac{R}{P} = \frac{1}{v}\frac{v}{T} = \frac{1}{T} \qquad \chi_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T = \frac{1}{v}\frac{RT}{P^2} = \frac{1}{P}$$

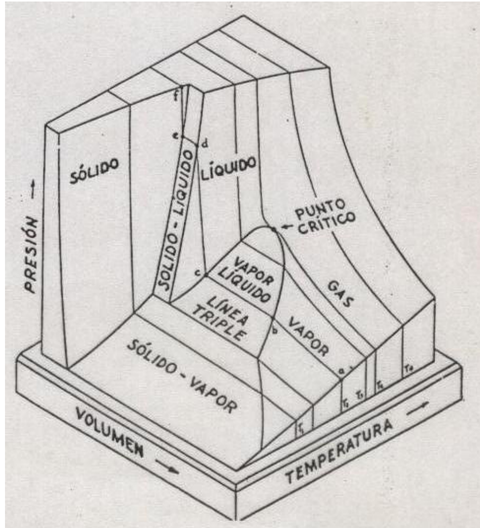
Llei de dalton

$$P = \sum_{i=1}^{N} P_i$$

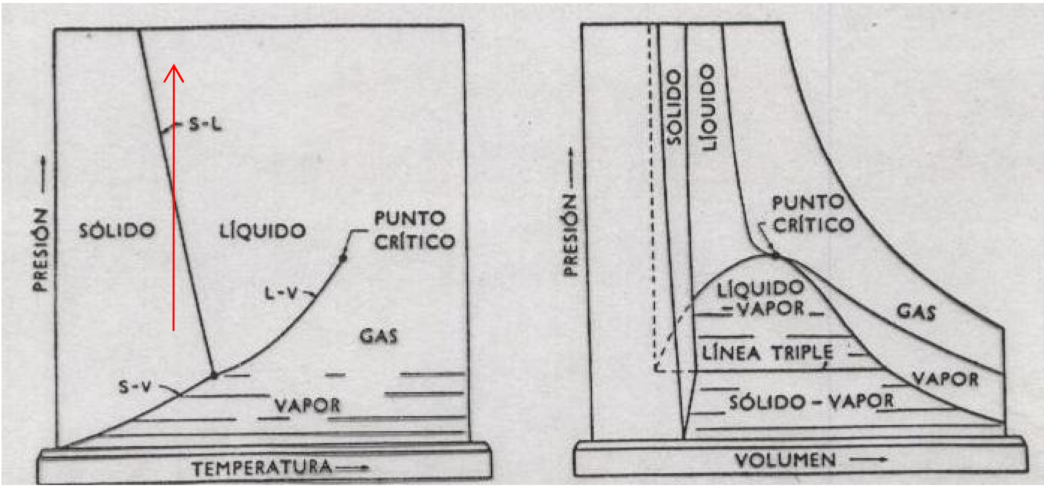
$$P_i = Px_i$$

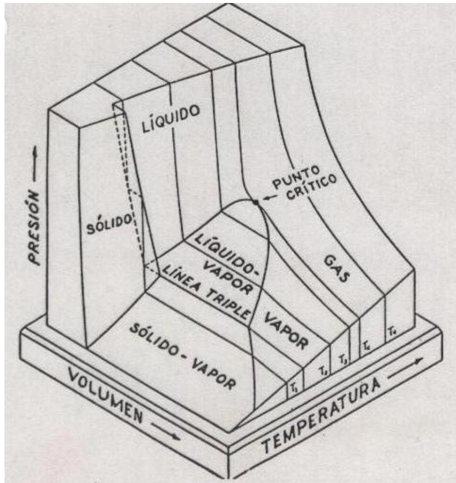
… i l'aigua?



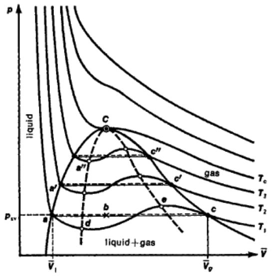


Aigua





El volum disminueix en la fusió!!



Equació de Van der Waals

$$\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT$$

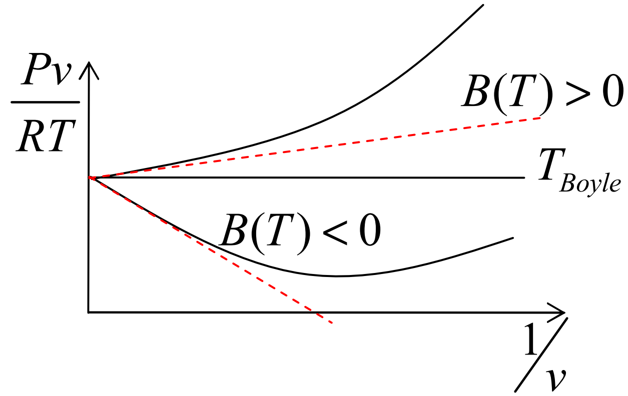
Desenvolupament del Virial

$$Pv = RT\left(1+\frac{B(T)}{v}+\frac{C(T)}{v^2}+\dots\right)$$

Temperatura de Boyle

$$\lim_{1/v\to 0}\frac{1}{RT}\left[\frac{\partial(Pv)}{\partial\left(1/v\right)}\right]_T = B(T)$$

$$B(T_{Boyle}) = 0$$



Dues opcions:

➢**Escriure l'equació d'estat en forma del virial**

➢Utilitzar la derivada i el limit

Coordenades del punt crític

$$\left(\frac{\partial P}{\partial v}\right)_{T_C} = \left(\frac{\partial^2 P}{\partial v^2}\right)_{T_C} = 0$$

Coordenades reduïdes

$$v_r = \frac{v}{v_C} \qquad T_r = \frac{T}{T_C} \qquad P_r = \frac{P}{P_C}$$

Substància A — estats corresponents — **Substància B**

Coordenades reals	Coordenades del P. crític	Coordenades reduïdes
P	P_c	$P_r = P/P_c$
V	V_c	$V_r = V/V_c$
T	T_c	$T_r = T/T_c$

Coordenades reduïdes	Coordenades reals	Coordenades del P. crític
$P_r = P'/P'_c$	P'	P'_c
$V_r = V'/V'_c$	V'	V'_c
$T_r = T'/T'_c$	T'	T'_c

$$\frac{P}{P_C} = \frac{P'}{P'_C} \qquad \frac{V}{V_C} = \frac{V'}{V'_C} \qquad \frac{T}{T_C} = \frac{T'}{T'_C}$$

Humitat absoluta

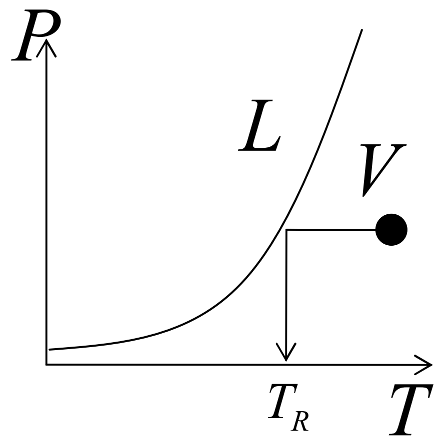
$$H_a = \frac{m_V}{V} = \frac{P_v M}{RT}$$

Humitat relativa

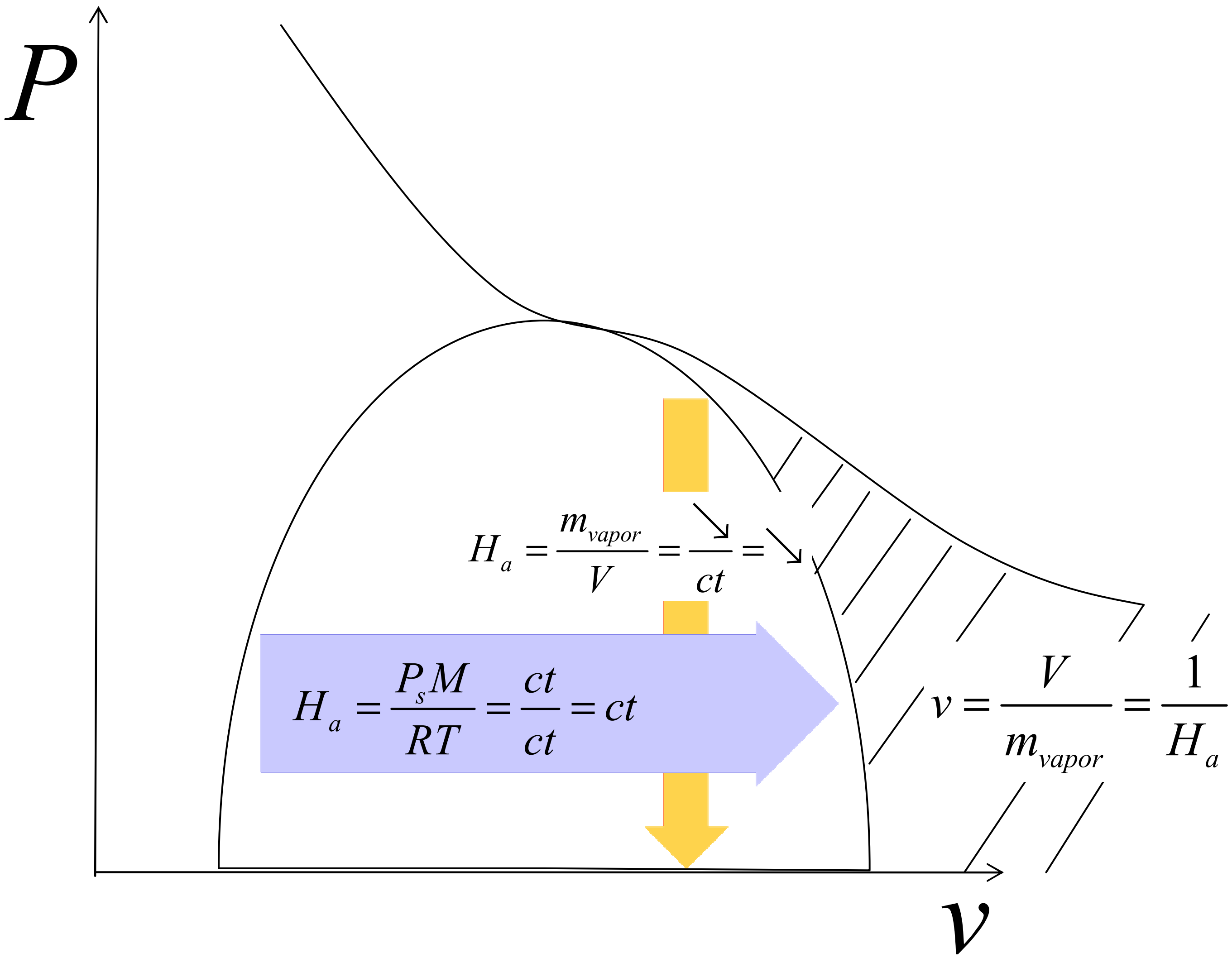
$$H_r = \frac{m_v}{m_s} = \frac{P_v}{P_S}$$

Temperatura de rosada

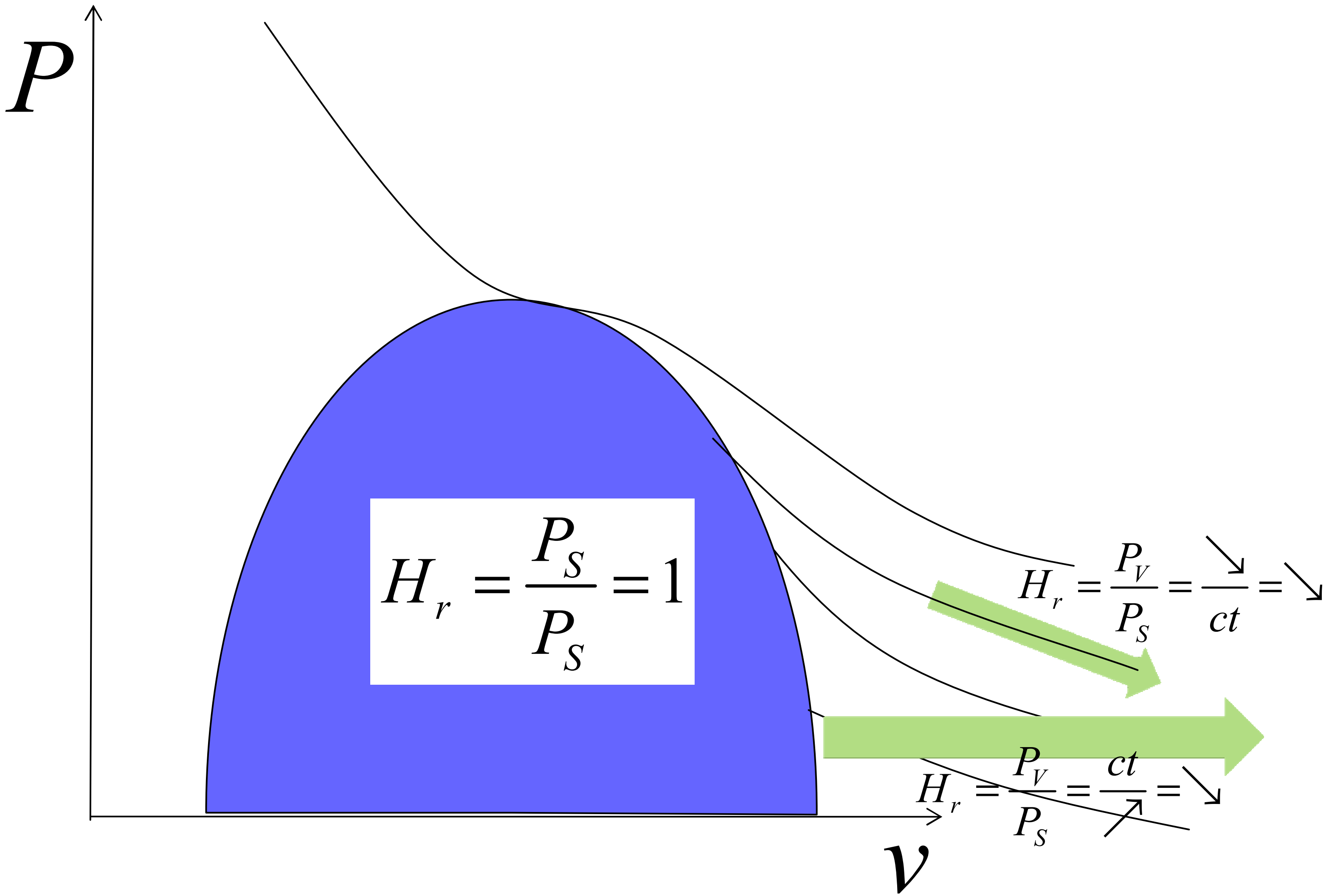
$$P_V = P_S(T_R)$$



Humitat absoluta

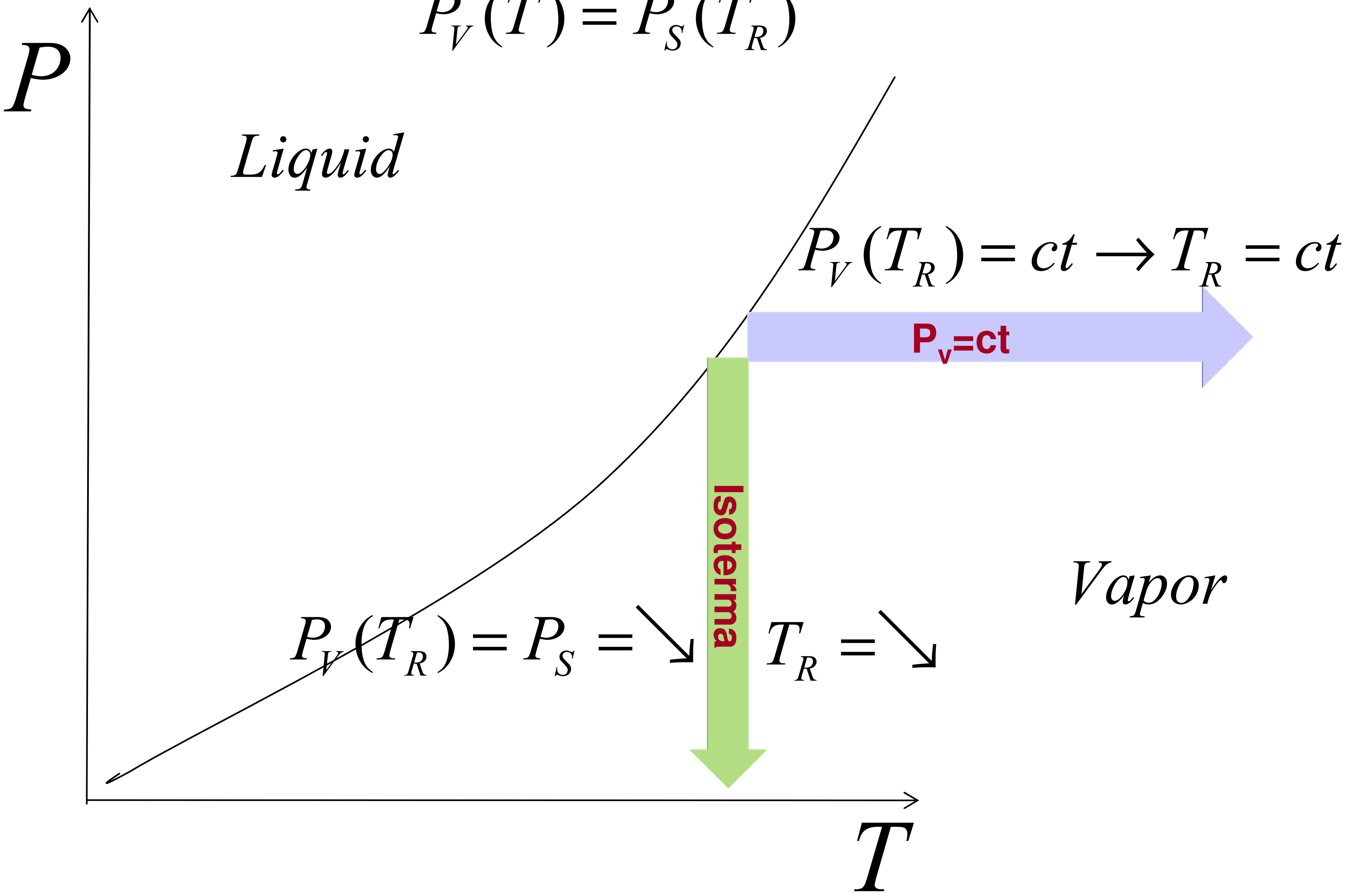


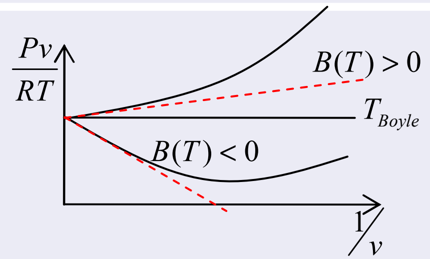
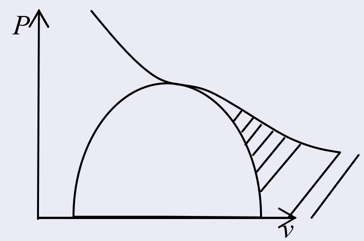
Humitat relativa



Temperatura de rosada

$$P_V(T) = P_S(T_R)$$



Gas ideal **Llei de Dalton**	$PV = nRT$ $P_i = Px_i$	
Virial **Temperatura de Boyle**	$Pv = RT\left(1+\frac{B(T)}{v}+\frac{C(T)}{v^2}+...\right)$ $B(T_{Boyle}) = 0$	
Estats corresponents	$P_r = \frac{P}{P_C}$	
Humitat	$H_a = \frac{m_V}{V} = \frac{P_v M}{RT}$ $H_r = \frac{P_v}{P_S}$	

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2.- Tema 2

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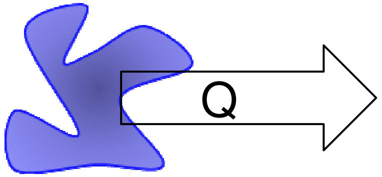
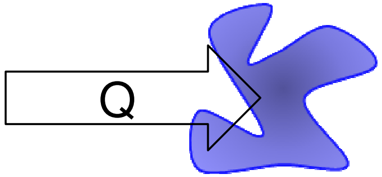
3.- Calor de canvi d'estat



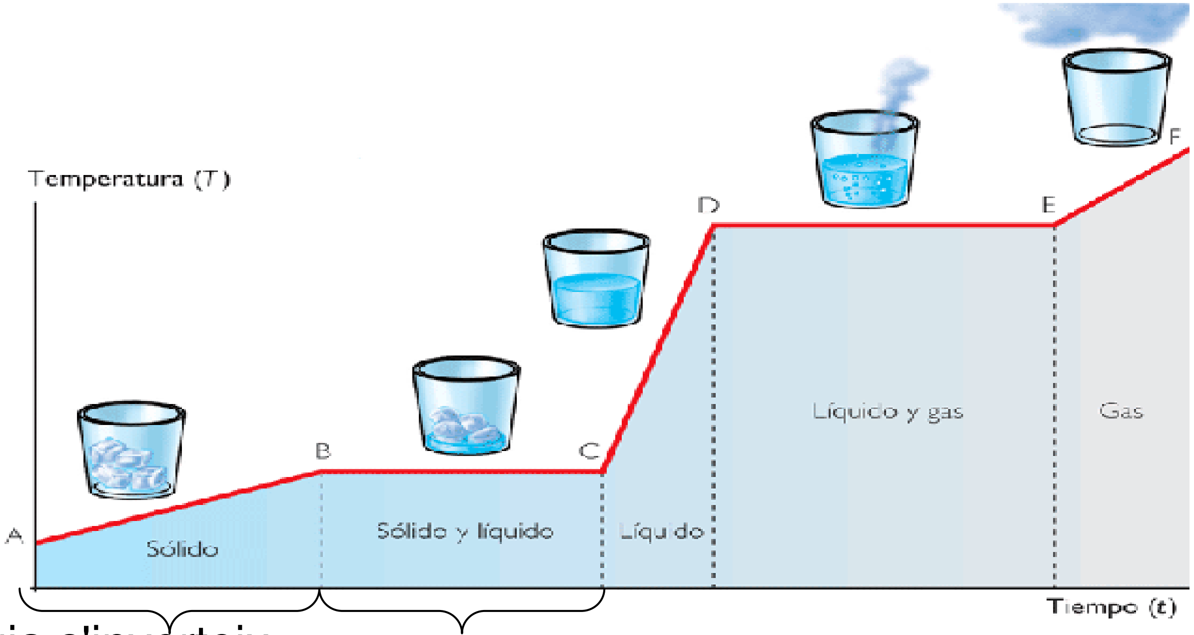
$Q < 0$

Procés exotèrmic



$Q > 0$

Procés endotèrmic



L'energia s'inverteix en escalfar

L'energia s'inverteix en canviar d'estat

$$Q = mc_e \Delta T$$

$$Q = \pm L m$$

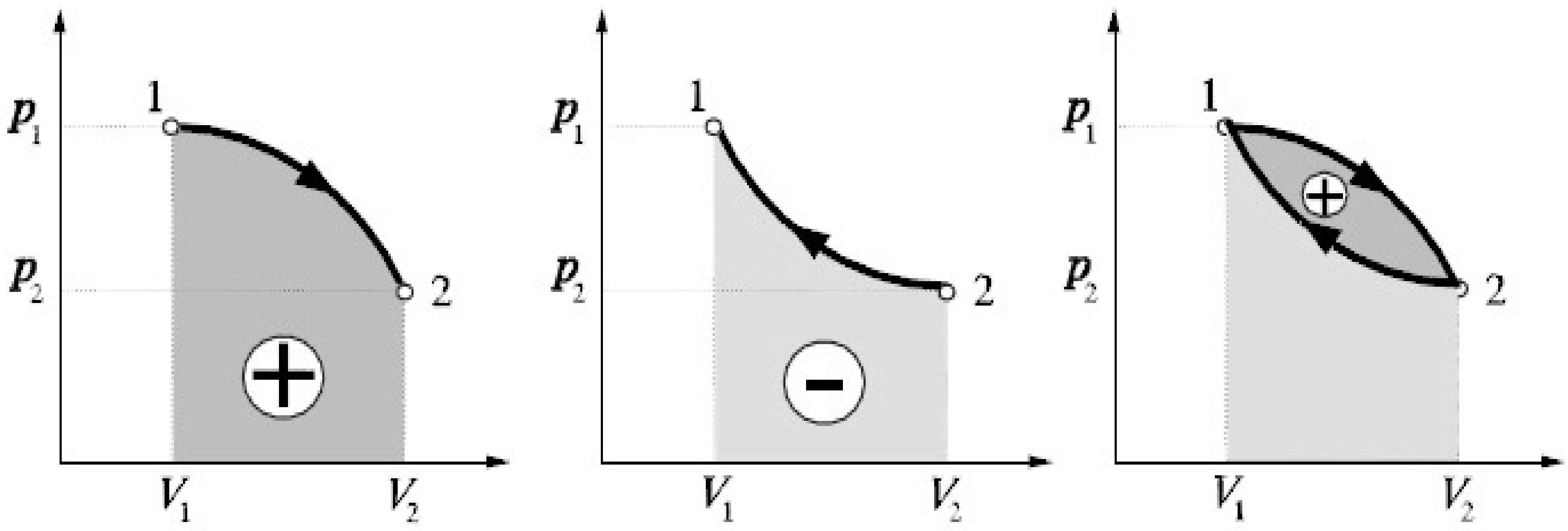
P3,P4,Q27,Q28,Q29

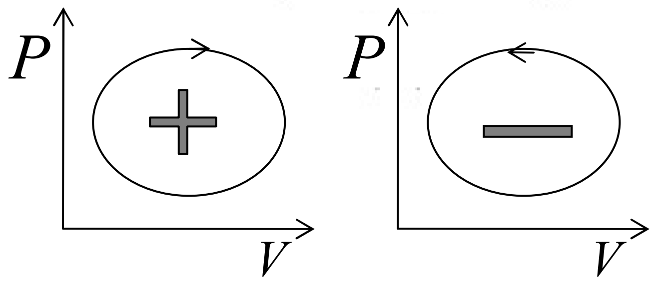
- El treball ve definit en un procés no en un estat (com la calor)
- Només en un procés reversible (= quasiestàtic) $P_{gas}=P_{ext}$!!

Interpretació gràfica:

Diagrama de Clapeyron

Si tenim un procés reversible $P=P_{ext}$





PROCESSOS REVERSIBLES (P=Pe)

Isòcor	Isòbar	Isoterm (g.i.)
$W = \int_{V_1}^{V_2} Pdv = 0$	$W = \int_{V_1}^{V_2} Pdv = P\Delta V$	$W = nRT \ln \frac{V_f}{V_i}$

$$W = \int_{V_1}^{V_2} PdV = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln \frac{V_f}{V_i}$$

PROCESSOS IRREVERSIBLES

no te sentit parlar de "isoterm", o "isobar".

No te sentit "dibuixar" el procés en un diagrama de Clapeyron

A volum constant	P_{ext}=constant i per tant $P_{fin}=P_{ext}$	en contacte amb una font a T a P_{ext} constant
$W = \int_{V_1}^{V_2} P_e dv = 0$	$W = \int_{V_1}^{V_2} P_e dv = P_e \Delta V$ Expansió contra el buit $W = 0 \cdot \Delta V = 0$	$W = P_2(V_2 - V_1) = P_2V_2 - P_2V_1$ $W = NRT\left(1 - \frac{V_1}{V_2}\right)$

$$W=\int PdV=\int P\left(V\alpha dT-V\chi_T dP\right)=\underbrace{\int PV\alpha dT}\underbrace{-PV\chi_T dP}$$

PROCÉS ISOBAR

$$W=\int PV\alpha dT$$

$$V=V_0e^{\alpha(T-T_0)}$$

$$W=V_0P\left(e^{\alpha(T_f-T_0)}-1\right)$$

$$V\approx V_0$$

$$W=V_0\alpha P\left(T_f-T_0\right)$$

PROCÉS ISOTERM

$$W=-\int PV\chi_T dP$$

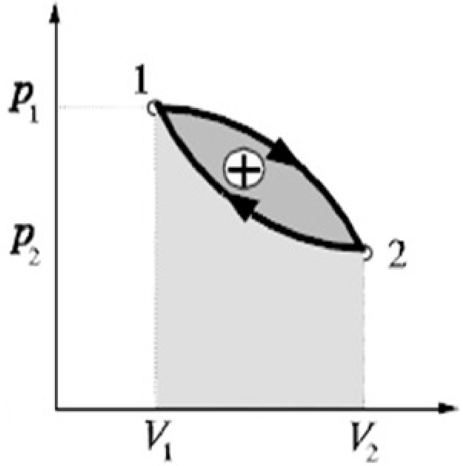
$$V=V_0e^{-\chi_T(P-P_i)}$$

$$W=V_0\left[P_fe^{-\chi_T(P_f-P_0)}-P_0\right]+\frac{V_0}{\chi_T}\left[e^{-\chi_T(P_f-P_0)}-1\right]$$

$$V\approx V_0$$

$$W=-\frac{V_0\chi_T}{2}\left(P_f^2-P_0^2\right)$$

$$dU = \delta Q - \delta W$$



En un cicle

$$\Delta U = 0$$

$$Q = W$$

$$\delta W = PdV$$

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

$$\delta Q = \delta W + dU$$

Relació de Mayer generalitzada

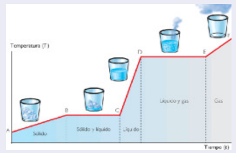
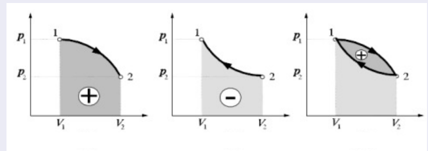
$$\left(\frac{\delta Q}{dT}\right)_P = C_P = C_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\alpha V$$

Entalpia

$$H \equiv U + PV$$

$$dH = \delta Q + VdP$$

Energia interna	Entalpia
$dU = \delta Q\big\rvert_V$	$dH = \delta Q\big\rvert_P$
$\left(\frac{\partial U}{\partial T}\right)_V = C_V$	$\left(\frac{\partial H}{\partial T}\right)_P = C_P$
$dU = C_V dT + f(v)$	$dH = C_P dT + f(P)$

Calor	$Q = mc_e \Delta T$ / $Q = \pm Lm$	
Treball	$W = \int_{V_1}^{V_2} P dv = 0$	
Treball en gasos reversible	$P = ct \rightarrow W = P\Delta V$ / $T = ct \rightarrow W = nRT \ln \frac{V_f}{V_i}$	
Treball en gasos irreversible	$P_{ext} = ct \rightarrow W = P_{ext}\Delta V$ / $T = ct \rightarrow W = ??$	
Treball en liq/sol app. linial	$W = V_0 \alpha P (T_f - T_0)$ / $W = -\frac{V_0 \chi_T}{2}(P_f^2 - P_0^2)$	
Primer principi	$dU = \delta Q - \delta W$ / $\left(\frac{\partial U}{\partial T}\right)_V = C_V$	
Entalpia	$H \equiv U + PV$ / $\left(\frac{\partial H}{\partial T}\right)_P = C_P$	