TEMA 1/2/3/4/5

$N_A = 6{,}023 \cdot 10^{23}$ /mol (cte de Av) 1 cal = 4,186 J

$S(\lambda U, \lambda V, \lambda n) = \lambda^{1} S(U,V,n)$

Ec. Gibbs

$dU = TdS - pdV + \mu dn$

$$\frac{\partial^2 u}{\partial s \partial v} = \frac{\partial^2 u}{\partial v \partial s} \rightarrow -\left(\frac{\partial p}{\partial s}\right)_v = \left(\frac{\partial T}{\partial v}\right)_s$$

s. aisl $\rightarrow$ $dU = 0$, $dV = 0$, $dn = 0$

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu}{T} dn$$

Coeficientes térmicos (s. cerrados)

$C_x = T\left(\frac{\partial S}{\partial T}\right)_x$ c_v, c_p

$\alpha_x = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_x$ α_p $\lambda_p = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_{p,n}$ $3\mu R$

$\chi_x = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_x$ χ_s, χ_T

$\beta_v = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_v$

$\gamma_v = \left(\frac{\partial p}{\partial T}\right)_v = \frac{\alpha_p}{\chi_T} = p\beta_v$

$v(T,p) \rightarrow dv = v(\alpha_p dT - \chi_T dp)$ $dT = \frac{1}{\alpha_p}\left(\chi_T dp + \frac{dv}{v}\right)$

$$dp = \frac{1}{\chi_T}\left(\alpha_p dT - \frac{dv}{v}\right)$$

G. id:

$\alpha_p = \frac{1}{T}$ $\chi_T = \frac{1}{p}$

NOTE BOOK

$dU = TdS - pdV + \mu dn$
$dF = -SdT - pdV + \mu dn$
$dH = TdS + Vdp + \mu n$

Relaciones de Maxwell:

$$\left(\frac{\partial S}{\partial p}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_S \qquad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

pavoyvotas patoyvotap
vapopates votapatov

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

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

Ecuaciones TdS:

$T,V \rightarrow TdS = C_V dT + T\frac{\alpha_p}{\chi_T} dV$

$T,p \rightarrow \quad = C_p\, dT - TV\alpha_p\, dp$

$V,p \rightarrow \quad = \frac{C_p}{V\alpha_p} dV + C_V \frac{\chi_T}{\alpha_p} dp$

$\frac{\chi_S}{\chi_T} = \frac{c_V}{c_p} \leq 1$

$\gamma = \frac{c_p}{c_V}$

Relación de Reech

$c_S = \frac{1}{\sqrt{\rho \chi_S}} \qquad \frac{\chi_S}{\chi_T}$

Relación de Mayer

$C_p = C_V + \frac{TV\alpha_p^2}{\chi_T} \qquad c_p \geq c_V$

G. id $\quad c_p = c_V + R$

$c_p - c_V = p\left(\frac{\partial V}{\partial T}\right)_p$

Ecuación de Euler

$U = TS - pV + \mu n$

$S = \frac{1}{T}U + \frac{p}{T}V - \frac{\mu}{T}n$

Sól.
$\alpha_p \propto c_p \quad p = \Gamma U/V$

$\Gamma = \frac{v\alpha_p}{c_V\chi_T} \rightarrow c_p = c_V(1 + T\alpha_p \Gamma)$

Gibbs-Duhem

$d\mu = -s\,dT + v\,dp \qquad \Sigma\, x_i\, d\mu_i$

TEMA 5

Gas ideal

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \qquad U = \frac{3}{2} nRT \quad \text{(monoat.)}$$

$$pV = nRT$$

$$S(U,V,n) = nR\left[\frac{5}{2} - \ln\sigma + \frac{3}{2}\frac{U}{n} + \ln\frac{V}{n}\right]$$

$$S(T,V,n) = nR\left[\frac{3}{2}\ln T + \ln\frac{V}{n}\right] + cte$$

$$S(T,p,n) = nR\left[\frac{5}{2}\ln T - \ln p\right] + cte$$

Hilo elástico ideal:

$$dU = TdS + \mathcal{Z}\,dL \qquad \lambda_{\mathcal{Z}} = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_{\mathcal{Z}} \quad Y_T = L\left(\frac{\partial \mathcal{Z}}{\partial L}\right)_T \quad C_{\mathcal{Z}} = T\left(\frac{\partial S}{\partial T}\right)_{\mathcal{Z}}$$

$$R.M \to \mathcal{Z} \leftrightarrow -p \qquad \left(\frac{\partial S}{\partial \mathcal{Z}}\right)_L = \left(\frac{\partial L}{\partial T}\right)_S \quad \left(\frac{\partial S}{\partial L}\right)_{\mathcal{Z}} = -\left(\frac{\partial \mathcal{Z}}{\partial T}\right)_S \quad \left(\frac{\partial S}{\partial \mathcal{Z}}\right)_T = \left(\frac{\partial L}{\partial T}\right)_{\mathcal{Z}}$$

$$C_{\mathcal{Z}} = C_L + TY_T L\lambda_{\mathcal{Z}}^2 \qquad \left(\frac{\partial S}{\partial L}\right)_T = -\left(\frac{\partial \mathcal{Z}}{\partial T}\right)_L$$

$$TdS = C_L\,dT - T\left(\frac{\partial \mathcal{Z}}{\partial T}\right)_L dL = C_{\mathcal{Z}}dT + T\left(\frac{\partial L}{\partial T}\right)_{\mathcal{Z}} d\mathcal{Z} = -T\left(\frac{\partial \mathcal{Z}}{\partial T}\right)_S dL + T\left(\frac{\partial L}{\partial T}\right)_S d\mathcal{Z}$$

$$\left(\frac{\partial U}{\partial L}\right)_T = T\left(\frac{\partial S}{\partial L}\right)_T + \mathcal{Z} = \mathcal{Z} - T\left(\frac{\partial \mathcal{Z}}{\partial T}\right)_L \quad ; \quad \left(\frac{\partial C_L}{\partial L}\right)_T = -T\left(\frac{\partial^2 \mathcal{Z}}{\partial T^2}\right)_L$$

→ ideal:

$$U = C_L T \qquad \left(\frac{\partial U}{\partial L}\right)_T = 0 \qquad dS = \frac{1}{T}dU - \frac{\mathcal{Z}}{T}dL$$

$$\mathcal{Z} = T f(L) = bT\left(\frac{L}{L_0} - 1\right) \qquad \lambda_T = -\frac{1}{T}\,\frac{L - L_0}{L}$$

$$\Delta S = C_L \ln\frac{U}{U_0} - \frac{bL_0}{2}\left(\frac{L}{L_0} - 1\right)^2 = C_L \ln\frac{T}{T_0} - \frac{bL_0}{2}\left(\frac{L}{L_0} - 1\right)^2$$

$$\mathcal{Z} = -T\left(\frac{\partial S}{\partial L}\right)_T$$

Radiación térmica:

$\phi = \varepsilon \sigma T^4$

$U = bVT^4$

$p = \frac{U}{3V} = \frac{b}{3} T^4$ $\quad \kappa_P / \cancel{c_P}$ $\quad \kappa_T \to \infty$

$S = \frac{1}{T} U + \frac{P}{T} V = \left(\frac{bV}{U}\right)^{1/4} = \frac{4}{3} b^{1/4} U^{3/4} V^{1/4} = \frac{4}{3} bVT^3$

$C_V = 3S = 4bVT^3$

TEMA 6

$S = k_B \ln q$ $\quad k_B = \frac{R}{N_A} = 1{,}38 \cdot 10^{-23}\ J/K$

$nR = N k_B$

• Hilo elástico

$\varepsilon = (L - L_0)/\Delta L_{max}$ $\quad 0 \sim 1$

$\left(\frac{dS}{nR}\right)_{U,n} = -(Z \Delta L_{max}/nRT)\, d\varepsilon = -\tilde{Z}\, d\varepsilon$ $\quad \tilde{Z} = \frac{Z \Delta L_{max}}{nRT}$

$S(L,n) = -nR(x_A \ln x_A + x_B \ln x_B)$ $\quad x_A = \frac{1+\varepsilon}{2}$ $\quad x_B = \frac{1-\varepsilon}{2}$

$\frac{S(\varepsilon)}{nR} = \ln 2 - \frac{1}{2}\left[\ln(1-\varepsilon^2) + 2\varepsilon \operatorname{arctanh} \varepsilon\right]$

$\varepsilon = \tanh \tilde{Z}$ $\quad \ln N! = N \ln N - N$

$\frac{s(\tilde{Z})}{R} = \ln(2\cosh \tilde{Z}) - \tilde{Z} \tanh \tilde{Z}$

• Disolución ideal

$U = n_1 u_1^0 + n_2 u_2^0$

$S = n_1 s_1^0 + n_2 s_2^0 + S_{mezcla} \rightarrow$ $\quad x_i = \frac{n_i}{n}$

$S_{mezcla} = -nR(x_1 \ln x_1 + x_2 \ln x_2)$

$\mu_i = \mu_i^0 + RT \ln x_i$

• Sólido paramagnético

$dU = TdS - \mu_0 V M dH + \mu dn$ $\quad m = \frac{M}{M_S}$ $\quad h = N_A \mu_0 \mu_m H$

$ds = \frac{1}{T} du + \frac{m}{T} dh$

$\chi_m = \left(\frac{\partial M}{\partial H}\right)_T$ $\quad$ no f. $\chi_m \neq \frac{M}{H}$ $\quad x_\uparrow = \frac{N_\uparrow}{N}$

$M_S = \cancel{N}\mu_m/V$

$M = (N_\uparrow - N_\downarrow)\mu_m/V = (x_\uparrow - x_\downarrow) M_S$ $\quad \varepsilon_\uparrow = -\mu_m \mu_0 H = -\varepsilon_\downarrow$

$U = N_\uparrow \varepsilon_\uparrow + N_\downarrow \varepsilon_\downarrow$

$u = -mh$

$s = -nR(x_\uparrow \ln x_\uparrow + x_\downarrow \ln x_\downarrow)$

$\frac{s(m)}{nR} = \ln 2 - \frac{1}{2}\left[\ln(1-m^2) + 2m \operatorname{arctanh} m\right]$

$m = \tanh(h/RT)$ $\quad c_H = R\left(\frac{h/RT}{\cosh(h/RT)}\right)^2$

$\frac{s(\tilde{h})}{R} = \ln(2\cosh \tilde{h}) - \tilde{h} \tanh \tilde{h}$

- **Gas ideal**

$\xi = N/N_c = N_A V_c / v \qquad \tilde{p} = p \dfrac{N_A V_c}{RT}$

$s = -nR\left[\ln \xi + \dfrac{1-\xi}{\xi}\ln(1-\xi)\right] \approx nR(1-\ln\xi)$

$\xi = 1 - e^{-\tilde{p}} \longrightarrow pv \approx RT$

$\dfrac{s(\tilde{p})}{R} = \dfrac{\tilde{p}}{e^{\tilde{p}}-1} - \ln(1-e^{-\tilde{p}})$

$s \approx R\left(1 - \ln\left(\dfrac{a u^{-3/2}}{v}\right)\right) = R\left(\ln v + \dfrac{3}{2}\ln u\right) + \text{cte}$

- **Sólido de Einstein**

$\Theta = \dfrac{\hbar\omega}{k_B} \qquad \varepsilon = u/3N_A\hbar\omega$

$\dfrac{ds}{3R} = \dfrac{\Theta}{T}\,d\varepsilon \qquad \dfrac{\Theta}{T} = \ln\dfrac{1+\varepsilon}{\varepsilon}$ Planck

$s \approx 3nR\left[(1+\varepsilon)\ln(1+\varepsilon) - \varepsilon\ln\varepsilon\right] \qquad u = 3R\Theta\varepsilon$

$c_v = 3R\left[\dfrac{(\Theta/2T)}{\sinh(\Theta/2T)}\right]^2$

- **Sólido ferromagnético** $\quad N = nN_A \to \mu m$; $\quad m = M/M_s$

$s(m) = \ln 2 - \dfrac{1}{2}\left[\ln(1-m^2) + 2m\,\text{arctanh}\, m\right]$

$u = -m\left(h + m\dfrac{RT_c}{2}\right)$

$RT = \dfrac{h + mRT_c}{\text{arctanh}\, m}$

NOTE BOOK

TEMA 7

$dU = TdS - pdV + \mu dn$ (cuasi)

dV_{alr} ✓ siempre

$\Delta S_{univ} = \Delta S + \Delta S_{alr} \geq 0$

<u>Proceso</u>

$\left.\begin{array}{l} đQ = TdS \\ đW = pdV \end{array}\right\}$ cuasi Q al sist. W del " $Q = \int$ $W = \int$

$dU = đQ - đW \rightarrow \Delta U = Q - W$ (sist. cerrado)

- no estático

$đW = -p_{alr} dV_{alr} = p_{alr} dV \rightarrow W = p^F \Delta V$ T, p

$đQ = -T_{alr} dS_{alr}$ $\Delta S^F = \frac{Q^F}{T^F} = -\frac{Q}{T_F}$

- ad.

$đQ = 0 \rightarrow (c) \rightarrow = TdS$

$\rightarrow (nc) \rightarrow \neq$

- cícl.

$Q = W$, $\Delta U = 0$

- <u>Politrópicos</u>

$đQ = C\,dT$

$n = \frac{C_x - C_p}{C_x - C_v} = \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_X$

$\left(\frac{\partial V}{\partial p}\right)_T dp = n\,dV$

$\left(\frac{\partial V}{\partial T}\right)_p dT = (1-n)\,dV$

$\left(\frac{\partial p}{\partial T}\right)_V dT = \frac{(n-1)}{n} dp$

G. id.:

$pV^n = cte$

TV^{n-1}

$Tp^{\frac{1-n}{n}}$

$\gamma = \frac{C_p}{C_v}$ ad.

no es. $W = \frac{p_2 V_2 - p_1 V_1}{1 - n}$

	A	P	T	V
Q	0	ΔH = $nc_p \Delta T$	W	ΔU
W	Y / $-\Delta U$	$p\Delta V$	$nRT \ln \frac{V_f}{V_i}$	0
ΔU	$nc_v \Delta T$ (g.i.)	$nc_v \Delta T$ / $Q - W$ "	0 (g.id.)	$nc_v \Delta T$
ΔS	≤ 0 / TdS	TdS	Q/T / TdS	$TdS_{(V,p)}$

TdS g.id. c_v

$\Delta S = c_v \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i} = c_p \ln \frac{T_f}{T_i} - nR \ln \frac{p_f}{p_i} = c_p \ln \frac{V_f}{V_i} + c_v \ln \frac{p_f}{p_i}$

Interacción térmica

$\Delta S_{univ} = \frac{Q_C}{T_C} + \frac{Q_F}{T_F} = Q_F\left(\frac{1}{T_F} - \frac{1}{T_C}\right)$

$Q_C + Q_F = 0$

$T = \frac{C_C T_C + C_F T_F}{C_C + C_F}$

$\Delta S = \Delta S_F + \Delta S_C = C_C \ln\frac{T}{T_C} + C_F \ln\frac{T}{T_F} \geq 0$

Entropía no compensada

$dS = d_eS + d_iS$

$d_eS \to \frac{dQ}{T_{alr}}$, $\quad d_iS \to \geq 0$

$N \equiv \Delta S - \int \frac{dQ}{T}$

Máquinas térmicas

$Q_{C \to STMA} = W + Q_{STMA \to F}$

$Q = W \qquad \eta = \frac{W}{Q_{C \to STMA}} = 1 - \frac{Q_{STMA \to F}}{Q_{C \to STMA}} \leq 1$

$K_{frig} = \frac{Q_{F \to STMA}}{W_{alr}} \qquad K_{calef} = \frac{Q_{STMA \to C}}{W_{alr}} = 1 + \frac{Q_{F \to STMA}}{W_{alr}} \geq 1$

Carnot

$\frac{Q_{ab}}{T_C} = -\frac{Q_{cd}}{T_F} \;\Big|\; \frac{Q_{C \to S}}{T_C} = \frac{Q_{S \to F}}{T_F} \to \Delta S_{univ} = 0$

$\eta_r = 1 - \frac{T_F}{T_C} \qquad K_{FRIG} = \frac{T_F}{T_C - T_F} \qquad K_{calr} = \frac{T_C}{T_C - T_F} = \frac{1}{\eta_r}$

$\neq$ Clausius

$\oint \frac{dQ}{T} \leq 0 \xrightarrow{(-1)} \Delta S_{univ} \geq 0$

Trabajo máx, Qmin (cuasi)

$W = Q - \underset{=0}{\Delta U}$

TEMA 8

Potenciales termodinámicos

U	S, V, n	$TS - pV + \mu n$	$TdS - pdV + \mu dn$
H	S, p, n	$U + pV = TS + \mu n$	$TdS + Vdp + \mu dn$
F	T, V, n	$U - TS = U - pV + \mu n$	$-SdT - pdV + \mu dn$
G	T, p, n	$\mu n = U + pV - TS$	$-SdT + Vdp + \mu dn$
Ψ_{GP}	T, V, μ	$-pV = U - TS - \mu n$	$-SdT - pdV - nd\mu$
			$nd\mu = -SdT + Vdp$
S	U, V, n	$\frac{1}{T}U + \frac{p}{T}V - \frac{\mu}{T}n$	$\frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dn$
			$n\, d\frac{\mu}{T} \ldots$

$H \quad c_p = T \cdot \left(\frac{\partial^2 H}{\partial S^2}\right)^{-1}$

$F \quad c_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_{V,n} \qquad \frac{1}{\chi_T} = V\left(\frac{\partial^2 F}{\partial V^2}\right)_{T,n}$

$G \quad c_p = -T \cdot \left(\frac{\partial^2 G}{\partial T^2}\right)_{p,n} \qquad \chi_T = -\left[\frac{\partial}{\partial p} \ln\left(\frac{\partial G}{\partial p}\right)_{T,n}\right]_{T,n} \qquad \Delta G = \Delta H - T\Delta S$

$\Psi \quad c_V = -T \cdot \left[\left(\frac{\partial^2 \Psi}{\partial T^2}\right)_{V,\mu} - \left(\frac{\partial^2 \Psi}{\partial T \partial \mu}\right)_V^2 \Big/ \left(\frac{\partial^2 \Psi}{\partial \mu^2}\right)_{T,V}\right]$

Ecuaciones Gibbs-Helmholtz

$S = -\left(\frac{\partial F}{\partial T}\right)_{V,n} \rightarrow \Delta S = -\left(\frac{\partial \Delta F}{\partial T}\right)_{V,n}$

$\Delta U = \left(\frac{\partial (\Delta F / T)}{\partial (1/T)}\right)_{V,n} \qquad U = \left(\frac{\partial (F/T)}{\partial (1/T)}\right)_{V,n}^{E.G.H.}$

$S = -\left(\frac{\partial G}{\partial T}\right)_{p,n} \rightarrow H = \left(\frac{\partial (G/T)}{\partial (1/T)}\right)_{p,n} \rightarrow \Delta$ Van't Hoff

$Q_{p_F} = \Delta H = \Delta U + p^F \Delta V$

$C_p = \left(\frac{\partial H}{\partial T}\right)_{p, n}$

E. disp $\quad A = U - T^F S \qquad W \leq -\Delta A \qquad Q \infty \Delta H$

$W \infty \Delta F$

E. lib $\qquad W \leq -\Delta F \leftrightarrow$

T. út. $\quad \Delta U = Q - W - W_{útil} \qquad T^F, p^F, \Delta S^F$

Ex. $\quad -W_{ut} = \Delta E \rightarrow E = U + p^F V - T^F S \qquad W_{ut} \leq -\Delta E$

G. $\quad -W_{ut} \geq \Delta G$

$H_1 = H_2 \rightarrow \mu_{J\text{-}K} = \left(\frac{\partial T}{\partial p}\right)_H \overset{\text{rev, isoH}}{=} \frac{v}{C_p}(T\alpha_p - 1)$

Sistemas magnéticos

$dU = TdS - \mu_0 V M dH$

- **Igualdad derivadas cruzadas** continuas

$$dz(x,y) = M(x,y)\,dx + N(x,y)\,dy$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \rightarrow \text{Relación de Maxwell}$$

- **Regla de la cadena**

$z(x,y)$
$z(x,w)$
$y(x,w)$

$$\rightarrow \left(\frac{\partial z}{\partial w}\right)_x = \left(\frac{\partial z}{\partial y}\right)_x \cdot \left(\frac{\partial y}{\partial w}\right)_x$$

$$\rightarrow \left(\frac{\partial z}{\partial x}\right)_w = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_w$$

- **Relación cíclica**

$$\left(\frac{\partial z}{\partial y}\right)_x = \frac{1}{\left(\frac{\partial y}{\partial z}\right)_x} \rightarrow \left(\frac{\partial z}{\partial y}\right)_x \cdot \left(\frac{\partial x}{\partial z}\right)_y \cdot \left(\frac{\partial y}{\partial x}\right)_z = -1$$

$$\operatorname{arctanh} x = \frac{1}{2}\ln\left(\frac{1+x}{1-x}\right)$$