TERMODINÁMICA y FÍSICA ESTADÍSTICA I

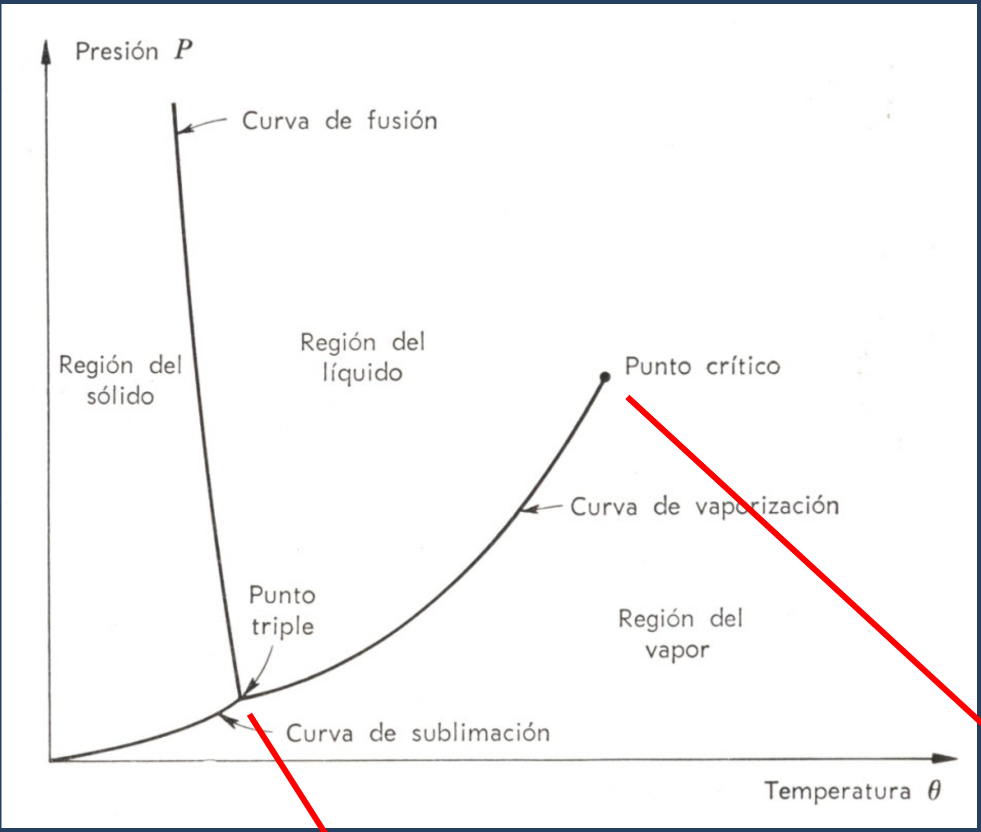
Tema 7 - APLICACIÓN DE LA TERMODINÁMICA A SUSTANCIAS PURAS

Diagramas de fases para sustancias puras. El punto crítico y las constantes críticas. Capacidades caloríficas molares. Expansión térmica de volumen. Compresibilidad isotérmica y adiabática.

BIBLIOGRAFÍA RECOMENDADA:

- Zemansky (7th ed.): Capítulos 9 y 13
- Zemansky (6ª ed.): Capítulos 2, 9 y 12

Diagramas PT y PV de una sustancia pura



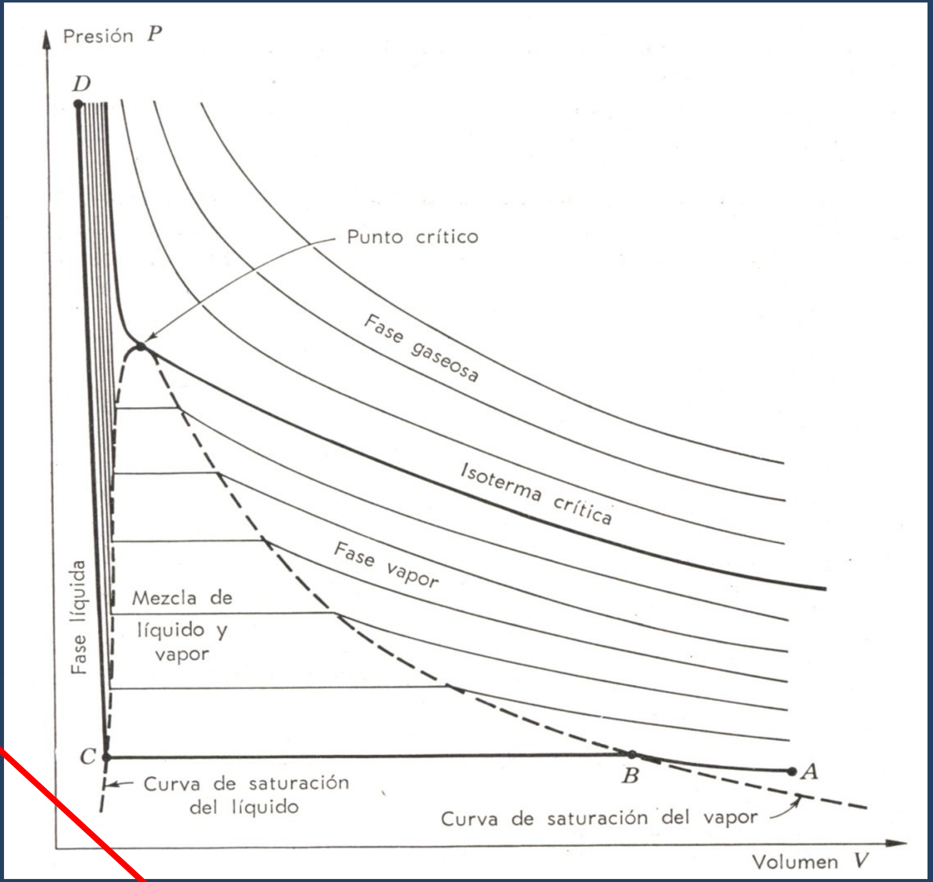


TABLE 9.2
Triple points of various substances

Substance	Temperature, K	Pressure, ~~MPa~~ kPa	Liquid density, kg/m^3
Hydrogen (normal)	13.80	7.042	77
Neon	24.56	50	1251
Oxygen	54.36	0.146	1306
Nitrogen	63.15	12.46	870
Carbon dioxide	216.6	518	1179
Water (H_2O)	273.16	0.612	999.78
Heavy water (D_2O)	276.97	0.661	1105.5

TABLE 9.1
Critical data

Substance	Temperature, K	Pressure, MPa	Density, kg/m^3
Helium-3	3.324	0.115	41.3
Helium-4	5.195	0.2275	69.64
Hydrogen (normal)	32.98	1.293	31.1
Nitrogen	126.20	3.390	313
Oxygen	154.58	5.043	436
Ammonia	405.5	11.35	236.4
Carbon dioxide	304.14	7.375	467.3
Water	647.067	22.0460	322.778

Diagrama de fases ρ–T del agua pura:
Curvas de densidad de agua líquida y en vapor

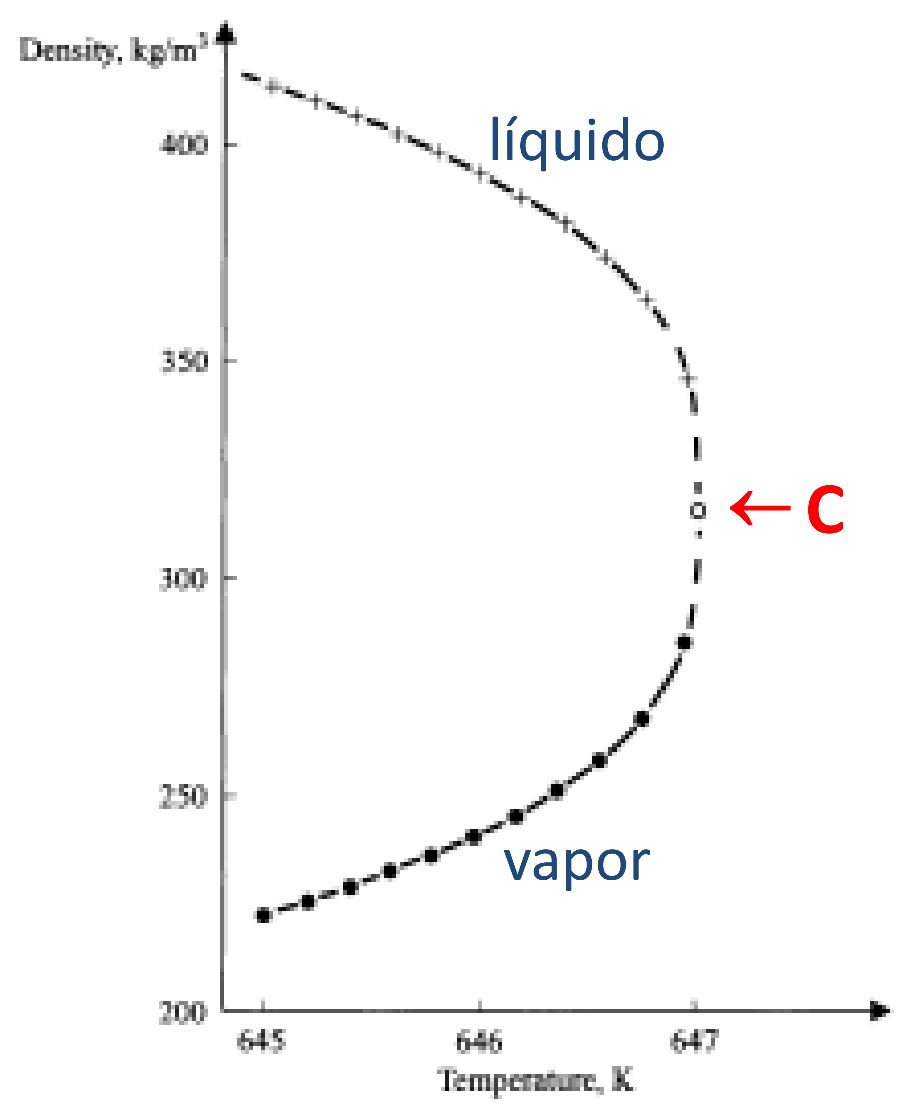


Diagrama de fases de diferentes sustancias puras

H_2O

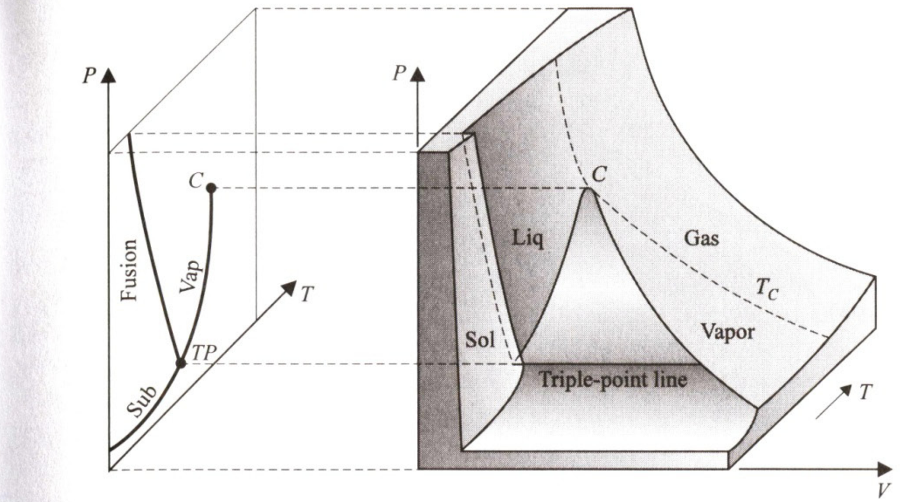


FIGURE 9-4
PVT surface for H_2O, which contracts while melting.

CO_2

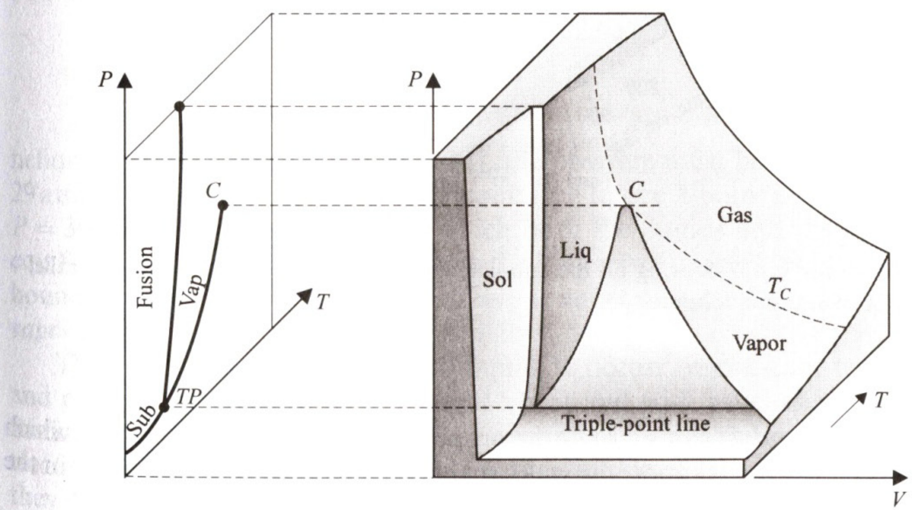


FIGURE 9-5
PVT surface for CO_2, which expands while melting.

Diagrama de fases del agua

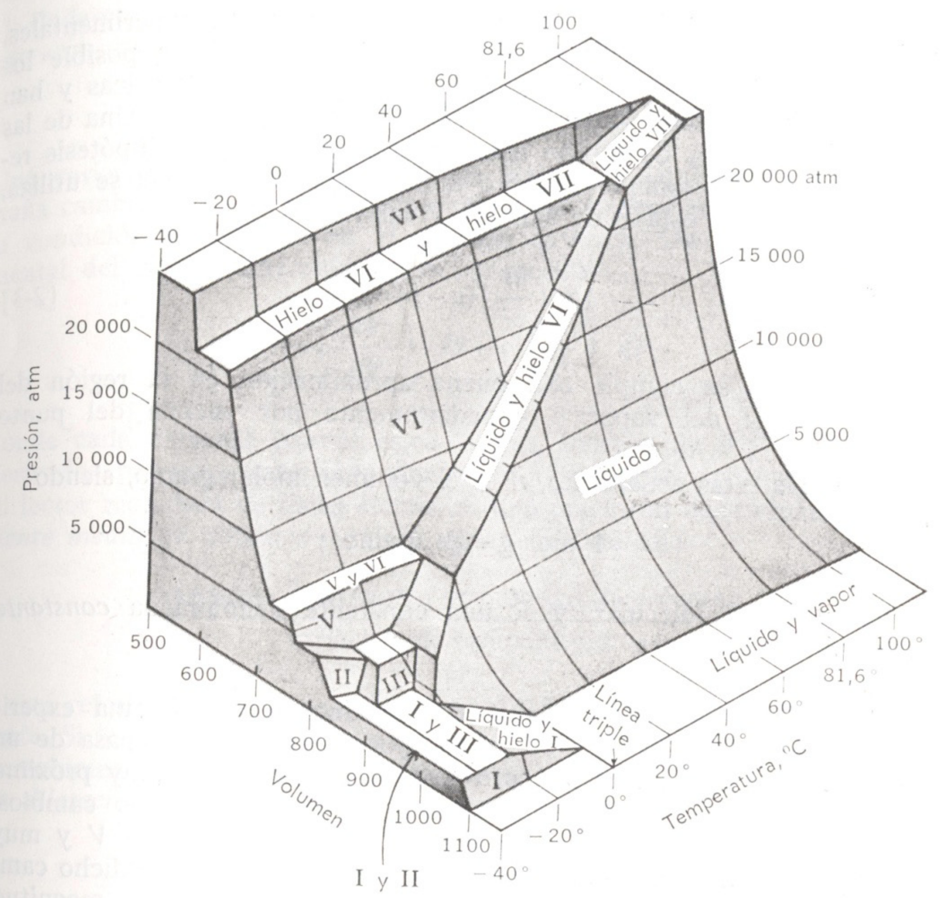
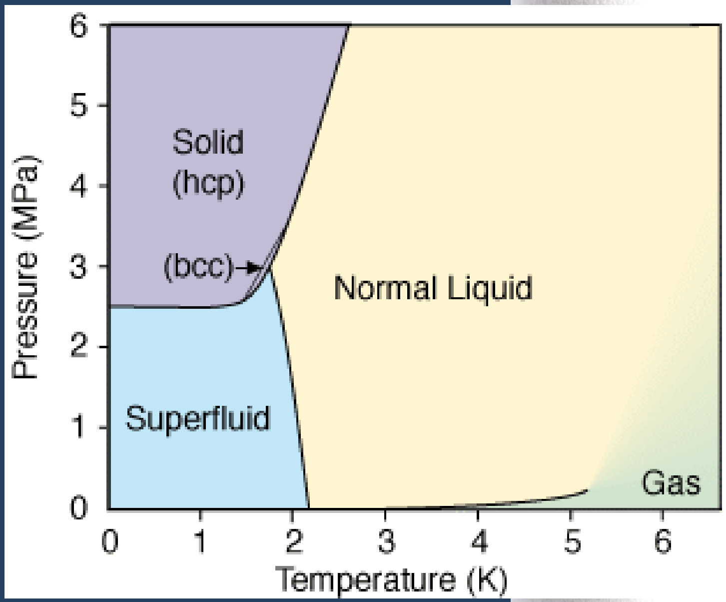


FIG. 2-5. Superficie *PVt* para el agua, en la que se muestran todos los puntos triples. (Construida por Verwiebe tomando como base las medidas de Bridgman.)

•http://en.wikipedia.org/wiki/Ice#Phases

Diagrama de fases del helio (^4He)



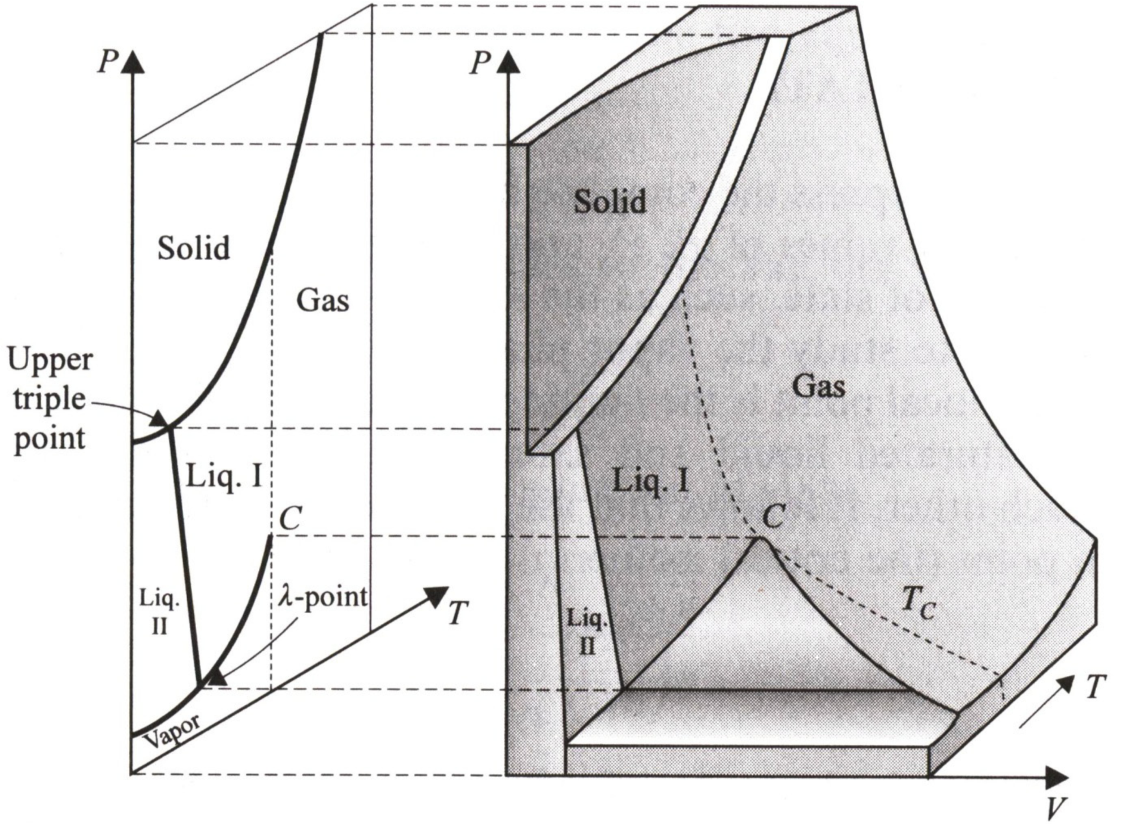


FIGURE 9-7
PVT surface and phase diagram for ^{4}He.

http://www.youtube.com/watch?v=2Z6UJbwxBZI

La ecuación de van der Waals y las constantes críticas

$$(P + \frac{a}{v^2}) \cdot (v - b) = RT$$

$$\left(\frac{\partial P}{\partial V}\right)_{T=T_c} = 0$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_c} = 0$$

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$\left(\frac{\partial P}{\partial V}\right)_{T=T_c} = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3} = 0$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_c} = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} = 0$$

$$P_c = \frac{a}{27b^2}$$

$$v_c = 3b$$

$$T_c = \frac{8a}{27bR}$$

$$p_r \equiv P / P_c ; v_r \equiv v / v_c ; T_r \equiv T / T_c$$

$$(p_r + \frac{3}{{v_r}^2}) \cdot (v_r - \frac{1}{3}) = \frac{8}{3} T_r$$

(Ley de los estados correspondientes)

La ecuación de van der Waals y las constantes críticas

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$$P_c = \frac{a}{27b^2} \qquad v_c = 3b \qquad T_c = \frac{8a}{27bR}$$

$$\left(p_r + \frac{3}{v_r^{\,2}}\right)\cdot\left(v_r - \frac{1}{3}\right) = \frac{8}{3}T_r$$

(Ley de los estados correspondientes)

$$\boxed{\frac{RT_c}{P_c v_c} = \frac{8}{3} > 1}$$

TABLE 9.4
Calculated values of RT_C/P_Cv_C

Substance	RT_C/P_Cv_C
Water	4.36
Ammonia	4.13
Carbon dioxide	3.64
Oxygen	3.49
Nitrogen	3.44
Helium	3.34
Hydrogen	3.26
Van der Waals gas	2.67
Ideal gas	1.00

Calores específicos: gases ideales

$$C_P = C_V + nR \quad \Rightarrow \quad c_P - c_V = R = 8.314 J/mol \cdot K$$

(Ley de Mayer para gases ideales)

- Gas ideal monoatómico:

$U = 3/2\ nRT$

$$\Rightarrow \quad c_V = \frac{1}{n}\left(\frac{dU}{dT}\right)_V = \frac{3}{2}R \rightarrow c_P = \frac{5}{2}R$$

- Gas ideal diatómico:

$U = 5/2\ nRT$

$$\Rightarrow \quad c_V = \frac{1}{n}\left(\frac{dU}{dT}\right)_V = \frac{5}{2}R \rightarrow c_P = \frac{7}{2}R$$

Calor específico real de gases diatómicos (H_2): ¡*efectos cuánticos*!

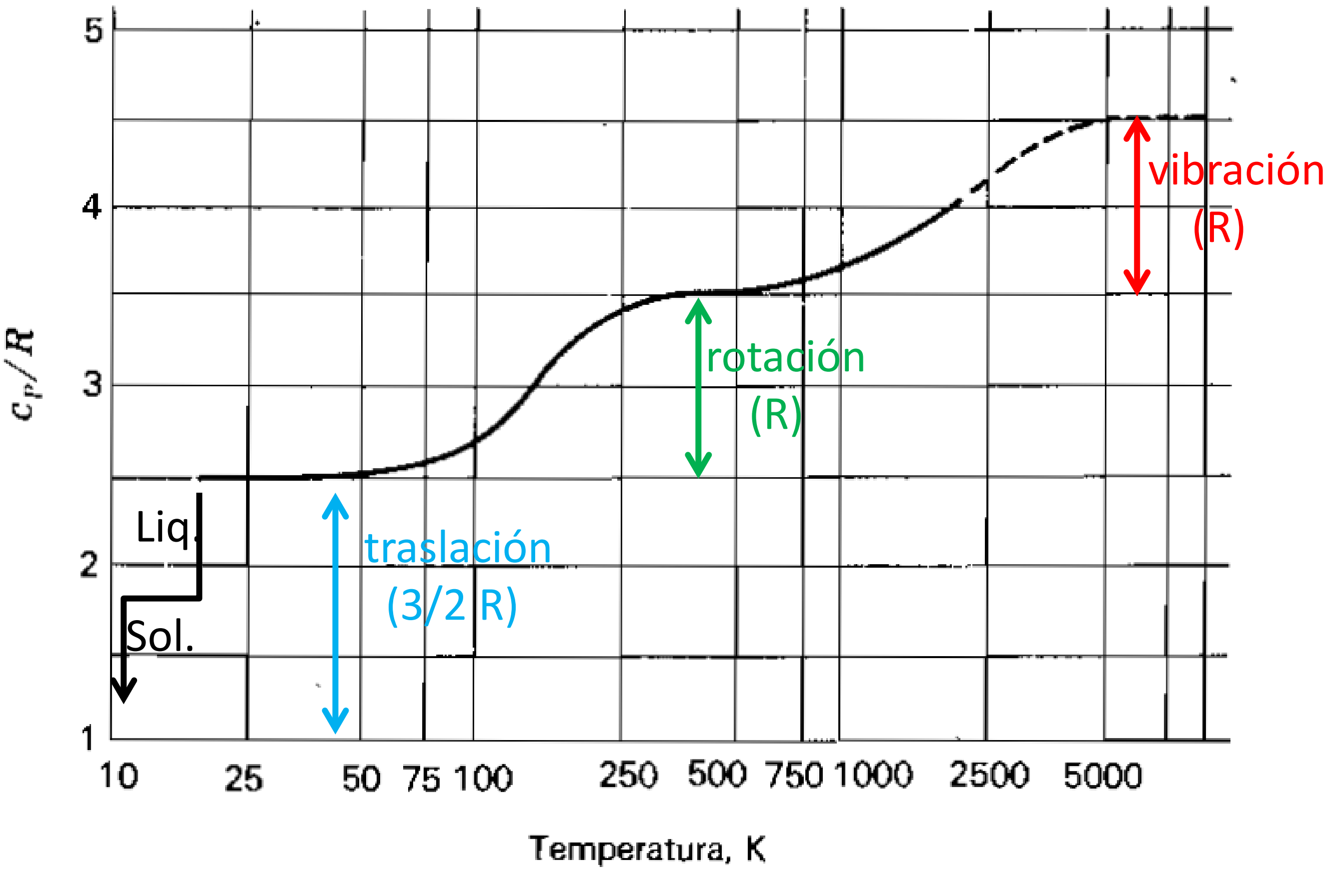


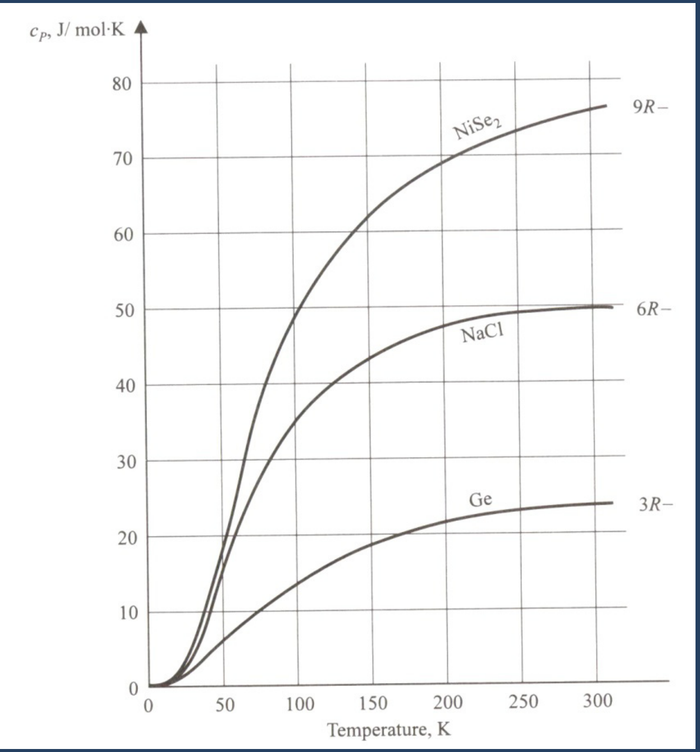
Figura 5.5. Valores experimentales de c_p/R en función de la temperatura para el hidrógeno, representados sobre escala logarítmica.

Calores específicos: sólidos

- Sólido de 3 dimensiones: **LEY de DULONG y PETIT**

$$U = \tfrac{1}{2} m v_x^2 + \tfrac{1}{2} m v_y^2 + \tfrac{1}{2} m v_z^2 + \tfrac{1}{2} k x^2 + \tfrac{1}{2} k y^2 + \tfrac{1}{2} k z^2 \rightarrow 6/2\, RT$$

$$\Rightarrow \quad c_V = \frac{1}{n}\left(\frac{dU}{dT}\right)_V = 3R = 24.9 J/mol \cdot K$$



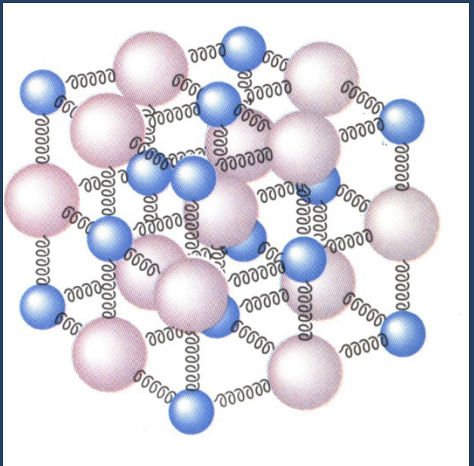


Figura 16-17 Modelo de un sólido en el que los átomos están conectados entre sí mediante muelles. La energía interna del sólido se compone de las energías de vibración cinética y potencial.

Calores específicos: sólidos

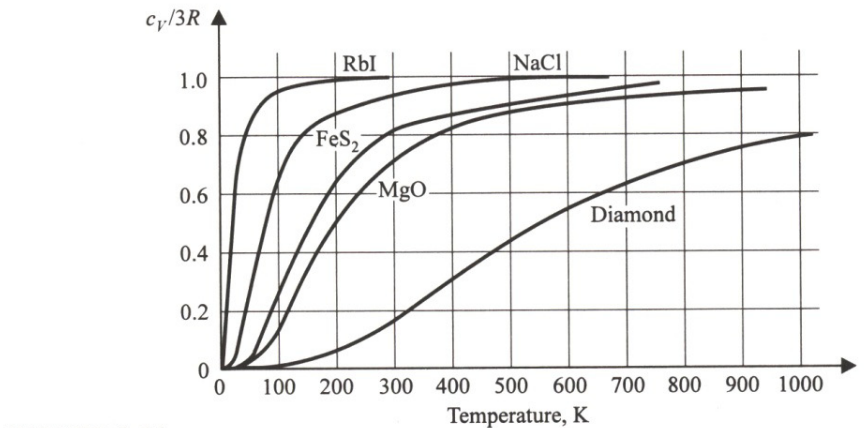
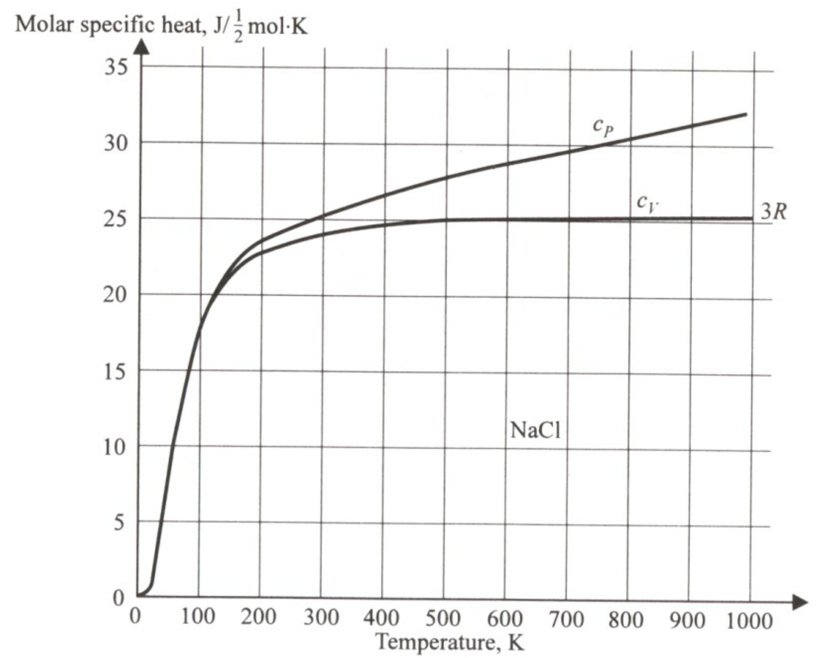
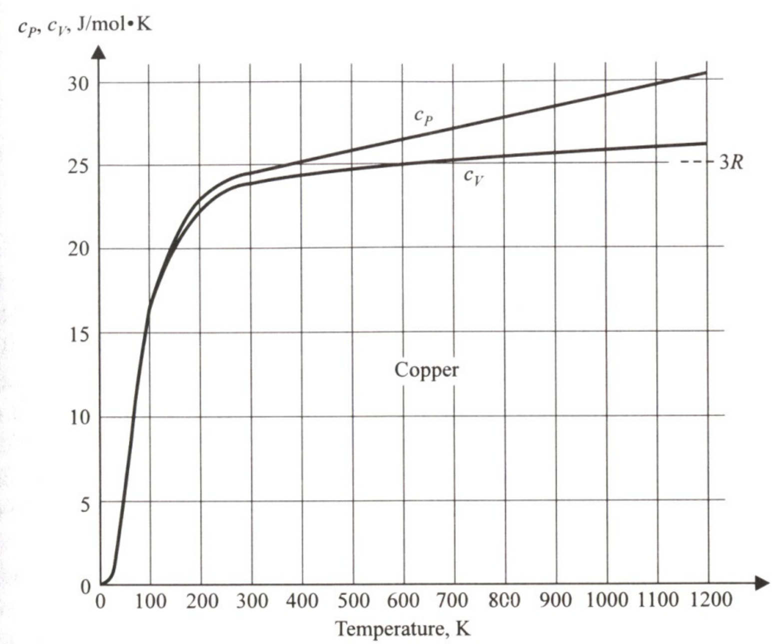


FIGURE 9-14
Temperature variation of $c_V/3R$ of nonmetals. (1 mol of diamond, $\frac{1}{2}$mol of RbI, NaCl, and MgO; and $\frac{1}{3}$mol of FeS_2.)





Dilatación térmica

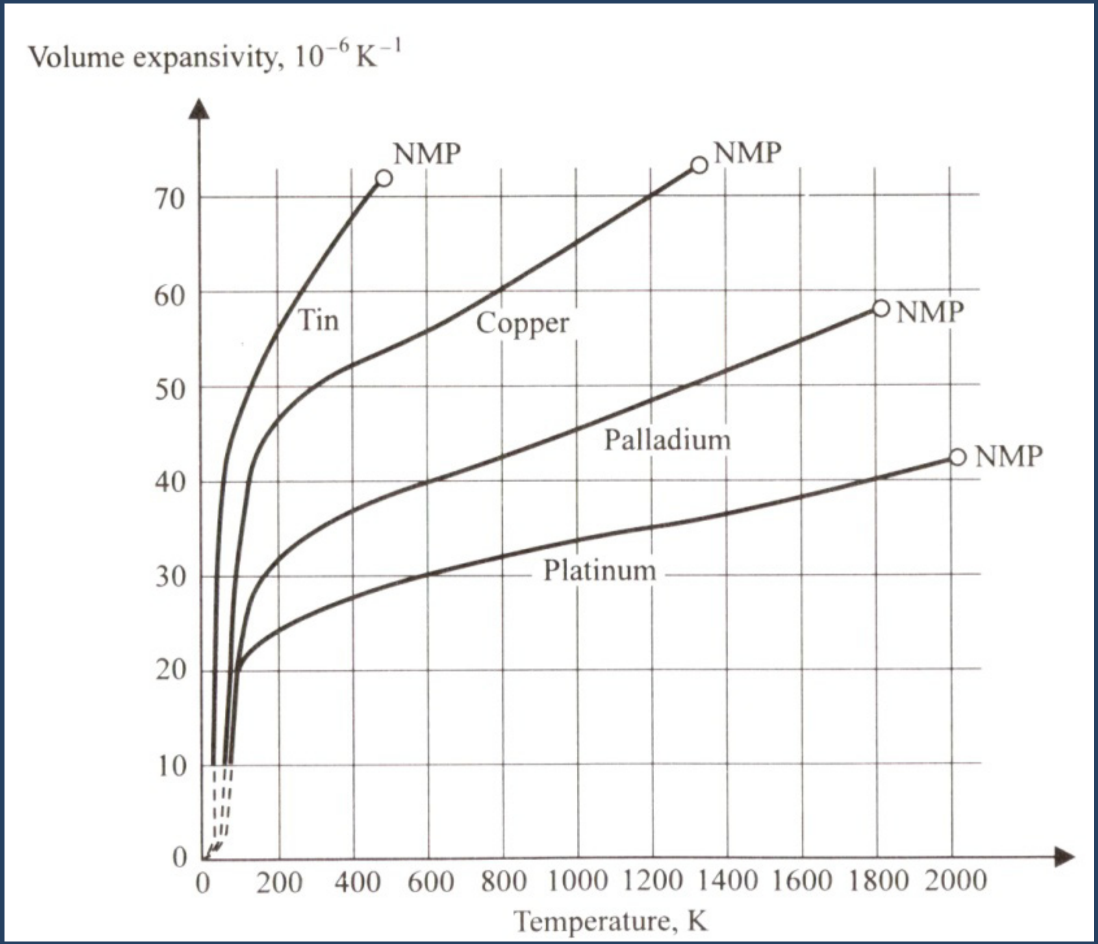
coeficiente de dilatación lineal

$$\alpha(T) = \lim_{\Delta T \to 0} \frac{1}{L}\frac{dL}{dT}$$

coeficiente de dilatación de volumen

$$\beta(T) = \lim_{\Delta T \to 0} \frac{1}{V}\frac{dV}{dT}$$

$$\beta = 3\alpha$$



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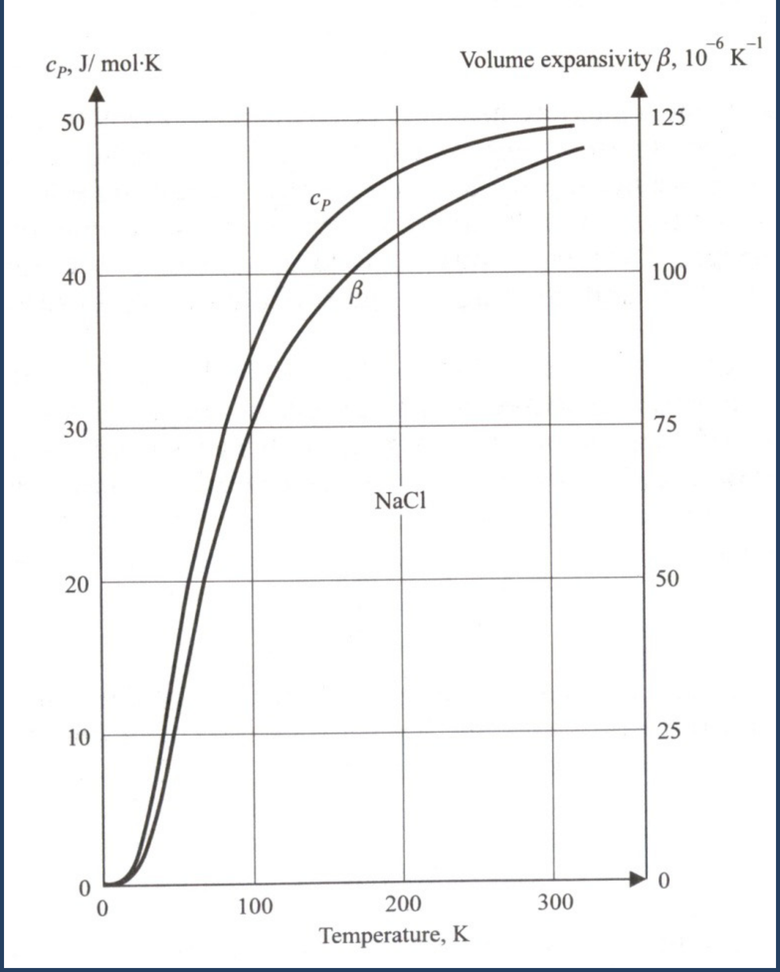
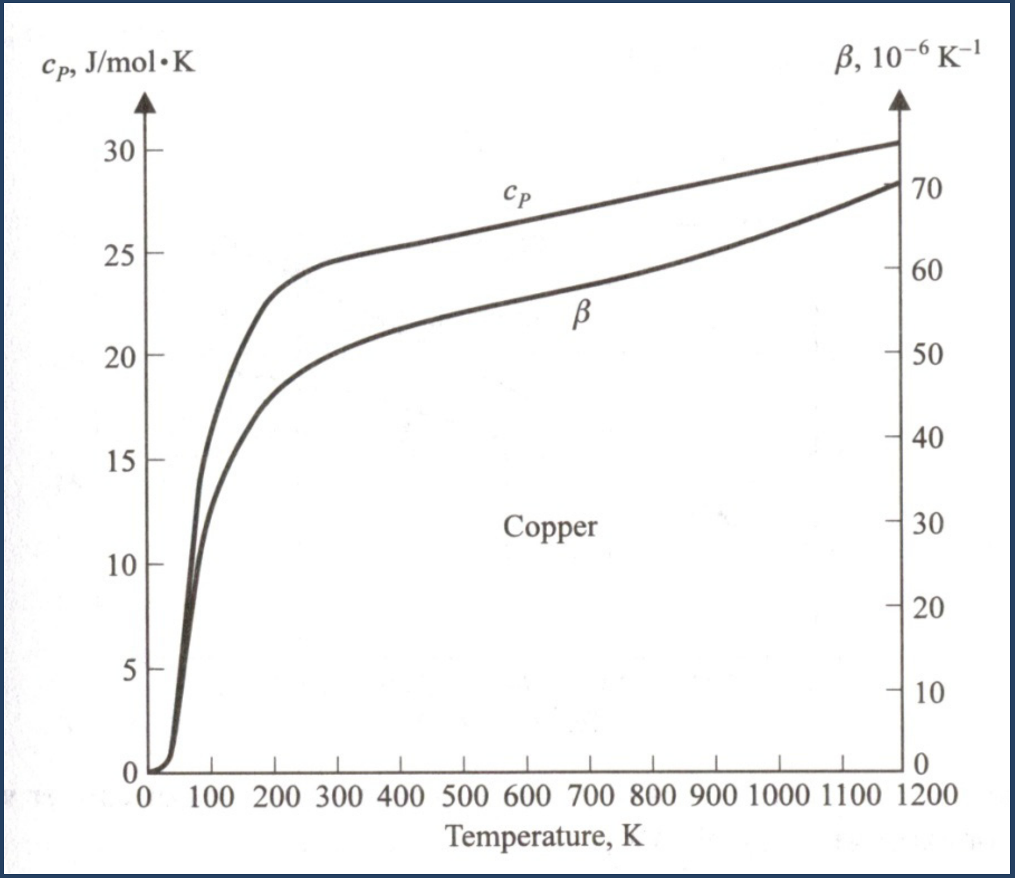




Compresibilidades adiabáticas e isotermas:

velocidad del sonido longitudinal en un gas ideal

$$B_S = \frac{1}{\kappa_S} = -V\left(\frac{\partial P}{\partial V}\right)_S = \gamma P \;\Rightarrow\; \kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S = \frac{1}{\gamma P}$$

$$v_s = \sqrt{\frac{B_S}{\rho}} = \sqrt{\frac{1}{\rho \kappa_S}} = \sqrt{\frac{\gamma P}{\rho}} = \sqrt{\frac{\gamma P v_m}{M}} \qquad \left(\rho = \frac{M}{v_m}\right)$$

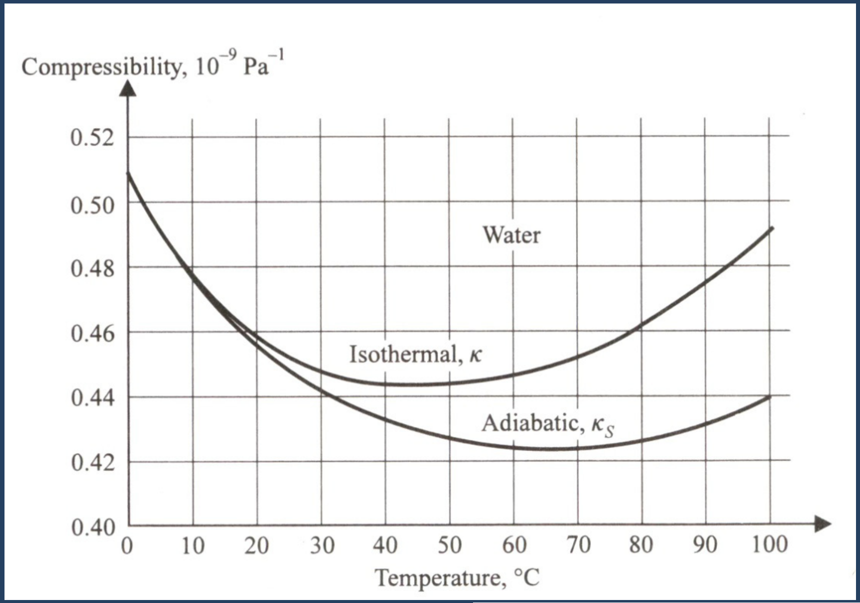
$$\Rightarrow \boxed{v_s = \sqrt{\frac{\gamma R T}{M}}}$$

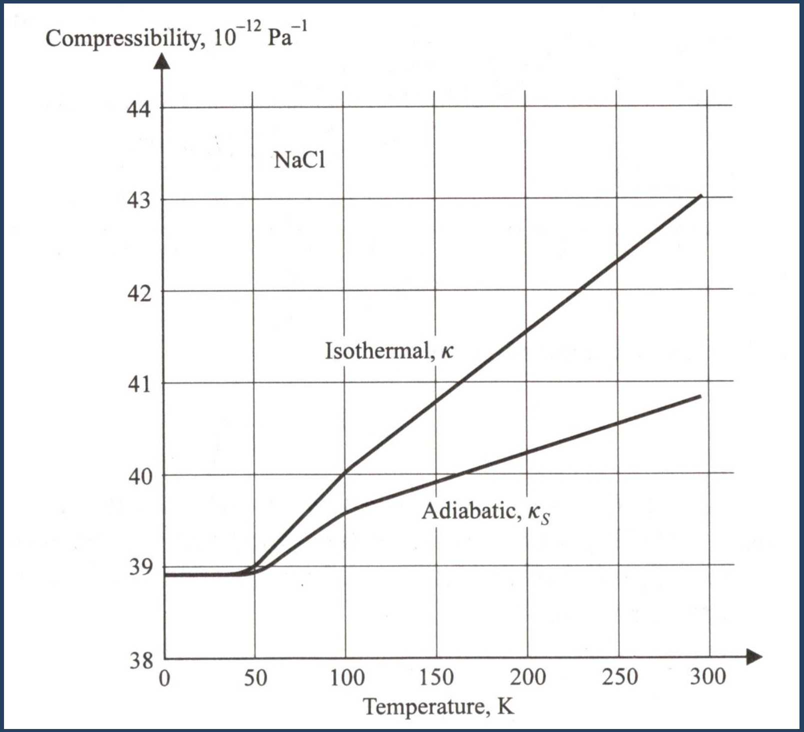
$$B = \frac{1}{\kappa} = -V\left(\frac{\partial P}{\partial V}\right)_T = P$$

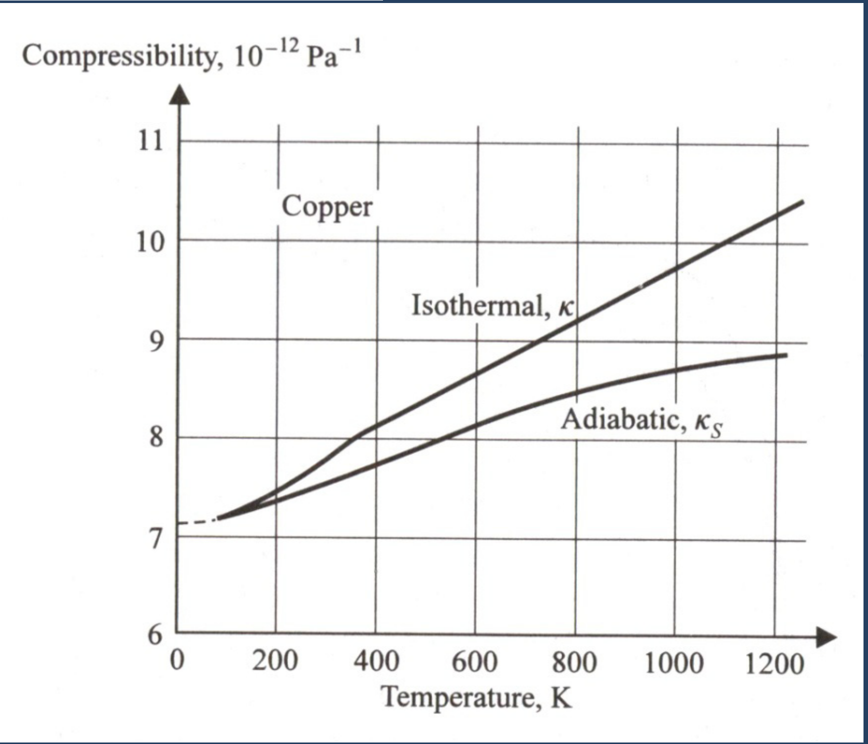
$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{P}$$

$$\Rightarrow \frac{\kappa}{\kappa_S} = \gamma \equiv \frac{c_P}{c_V}$$

Compresibilidades adiabáticas e isotermas







Relaciones generales entre coeficientes termodinámicos

$$\left(c_P - c_V\right) = \frac{Tv\beta^2}{\kappa}$$

$$\frac{\kappa}{\kappa_S} = \frac{c_P}{c_V} \equiv \gamma$$

$$\left(\kappa - \kappa_S\right) = \frac{Tv\beta^2}{c_p}$$