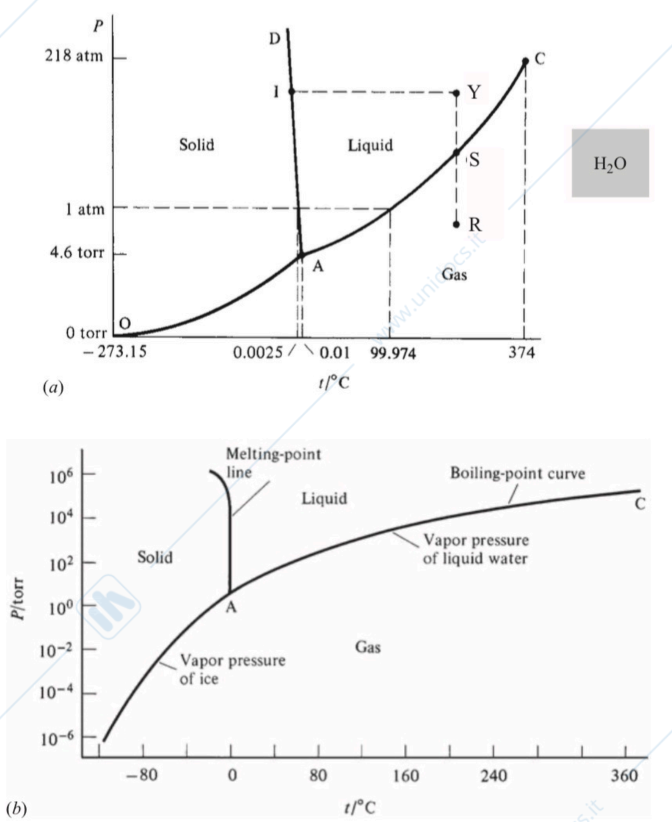
Equilibrio di fase



Il numero di gradi di libertà (varianza), f, di un sistema all'equilibrio è il numero di variabili intensive che bisogna specificare per definire il suo stato

Cominciamo con il considerare un sistema dove non avvengano reazioni chimiche e che ogni specie sia presente in ogni fase.

Indichiamo con "c" il numero di specie chimiche e con "p" il numero di fasi. Quindi in ogni fase ci sono:

pc frazioni molari

consideriamo anche la Temperatura e la pressione

$pc + 2$

per la relazione che lega le frazioni molari:

$$x_1^\alpha + x_2^\alpha + x_3^\alpha + \dots + x_c^\alpha = 1$$

Questa equazione vale per ogni fase.

Quindi pc + 2 non sono tutte variabili indipendenti.

Alla equazione delle frazioni molari abbiamo anche le equazioni di uguaglianza dei potenziali chimici

$$\mu_1^\alpha = \mu_1^\beta = \mu_1^\gamma = \dots$$

$$\mu_2^\alpha = \mu_2^\beta = \mu_2^\gamma = \dots$$

$$- \quad - \quad - \quad - \quad - \quad -$$

$$\mu_c^\alpha = \mu_c^\beta = \mu_c^\gamma = \dots$$

Siccome siamo in presenza di "p" fasi avremo

$p-1$ uguaglianze

e

$p-1$ eq. indipendenti

le specie chimiche sono "c" avremo

$c(p-1)$ uguaglianze sui potenziali chimici

Quindi

$$f = pc+2-p-c(p-1)$$

$$f = c-p+2$$

In presenza di reazioni chimiche

$$f = c - p + 2 - r$$

oltre alle reazioni chimiche possono esserci vincoli stechiometrici

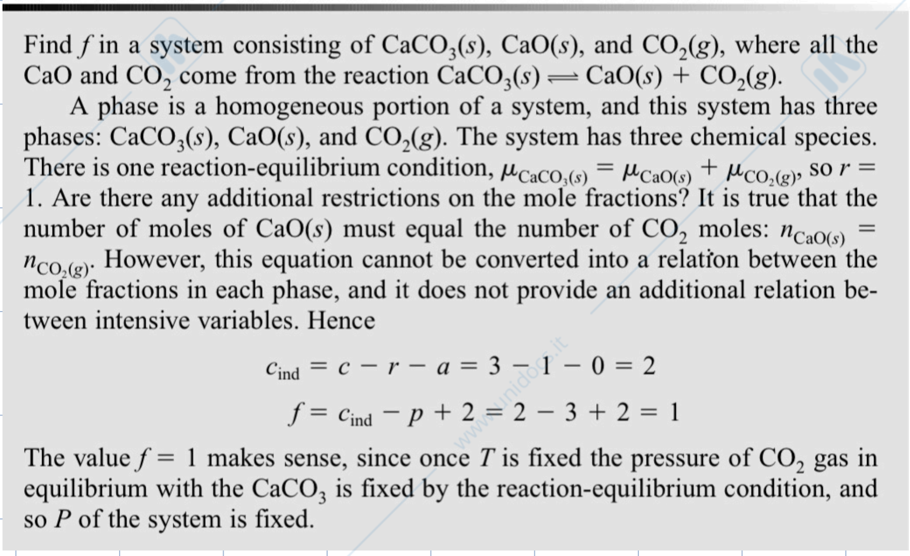
$$2\,NH_3 \rightleftarrows N_2 + 3\,H_2$$

$$f = c - p + 2 - r - a$$

$$C_{ind} = c - r - a$$

$$f = C_{ind} - p + 2$$

Esempio



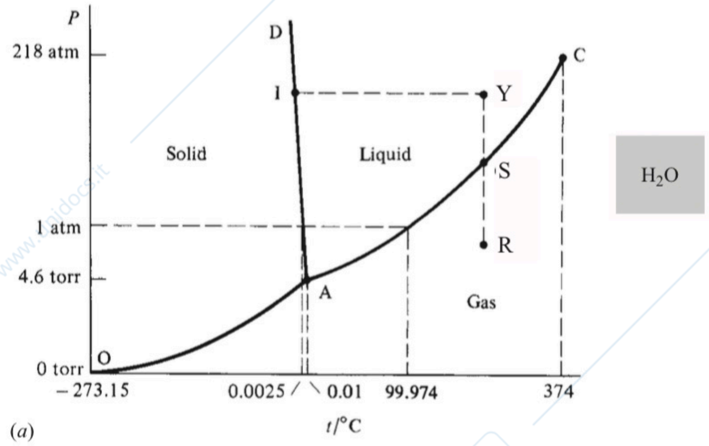
Find f in a system consisting of $CaCO_3(s)$, $CaO(s)$, and $CO_2(g)$, where all the CaO and CO_2 come from the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$.

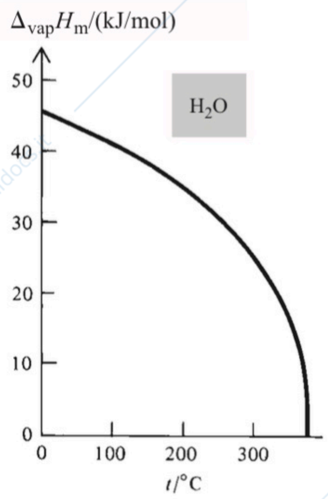
A phase is a homogeneous portion of a system, and this system has three phases: $CaCO_3(s)$, $CaO(s)$, and $CO_2(g)$. The system has three chemical species. There is one reaction-equilibrium condition, $\mu_{CaCO_3(s)} = \mu_{CaO(s)} + \mu_{CO_2(g)}$, so $r = 1$. Are there any additional restrictions on the mole fractions? It is true that the number of moles of $CaO(s)$ must equal the number of CO_2 moles: $n_{CaO(s)} = n_{CO_2(g)}$. However, this equation cannot be converted into a relation between the mole fractions in each phase, and it does not provide an additional relation between intensive variables. Hence

$$c_{ind} = c - r - a = 3 - 1 - 0 = 2$$

$$f = c_{ind} - p + 2 = 2 - 3 + 2 = 1$$

The value $f = 1$ makes sense, since once T is fixed the pressure of CO_2 gas in equilibrium with the $CaCO_3$ is fixed by the reaction-equilibrium condition, and so P of the system is fixed.





An approximate rule for relating enthalpies and entropies of liquids to those of gases is **Trouton's rule,** which states that $\Delta_{vap}S_{m,nbp}$ for vaporization of a liquid at its normal boiling point (nbp) is roughly $10\frac{1}{2}R$:

$$\Delta_{vap}S_{m,nbp} = \Delta_{vap}H_{m,nbp}/T_{nbp} \approx 10\tfrac{1}{2}\,R = 21 \text{ cal/(mol K)} = 87 \text{ J/(mol K)}$$

Trouton's rule fails for highly polar liquids (especially hydrogen-bonded liquids) and for liquids boiling below 150 K or above 1000 K (see Table 7.1). The accuracy of Trouton's rule can be improved substantially by taking

$$\Delta_{vap}S_{m,nbp} \approx 4.5R + R\ln(T_{nbp}/\text{K}) \qquad (7.12)$$

TABLE 7.1

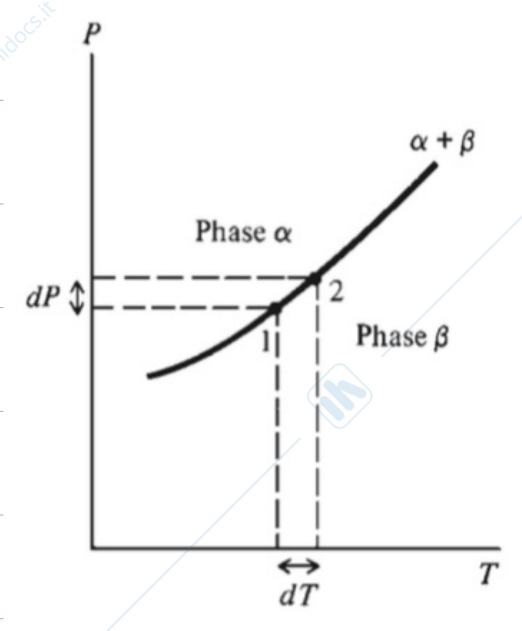
Enthalpies and Entropies of Fusion and Vaporization[a]

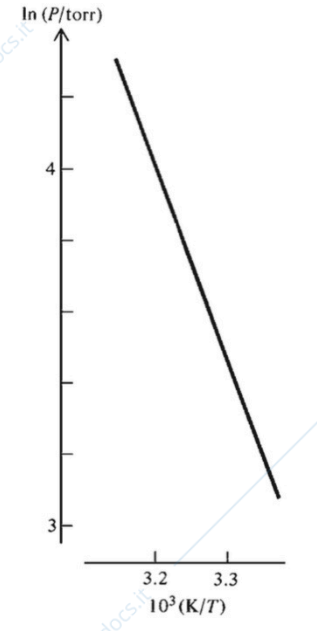
Substance	T_{nmp} K	$\Delta_{fus}H_m$ kJ/mol	$\Delta_{fus}S_m$ J/(mol K)	T_{nbp} K	$\Delta_{vap}H_m$ kJ/mol	$\Delta_{vap}S_m$ J/(mol K)	$\Delta_{vap}S_m^{THE}$ J/(mol K)
Ne	24.5	0.335	13.6	27.1	1.76	65.0	64.8
N_2	63.3	0.72	11.4	77.4	5.58	72.1	73.6
Ar	83.8	1.21	14.4	87.3	6.53	74.8	74.6
C_2H_6	89.9	2.86	31.8	184.5	14.71	79.7	80.8
$(C_2H_5)_2O$	156.9	7.27	46.4	307.7	26.7	86.8	85.1
NH_3	195.4	5.65	28.9	239.7	23.3	97.4	83.0
CCl_4	250.	2.47	9.9	349.7	30.0	85.8	86.1
H_2O	273.2	6.01	22.0	373.1	40.66	109.0	86.7
I_2	386.8	15.5	40.1	457.5	41.8	91.4	88.3
Zn	693.	7.38	10.7	1184.	115.6	97.6	96.3
NaCl	1074.	28.2	26.2	1738.	171.	98.4	99.4

[a] $\Delta_{fus}H_m$ and $\Delta_{fus}S_m$ are at the normal melting point (nmp). $\Delta_{vap}H_m$ and $\Delta_{vap}S_m$ are at the normal boiling point (nbp). $\Delta_{vap}S_m^{THE}$ is the normal-boiling-point $\Delta_{vap}S_m$ value predicted by the Trouton–Hildebrand–Everett rule.

Eq. di Clausius-Clapeyron

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V}$$





Equilibrio solido-solido

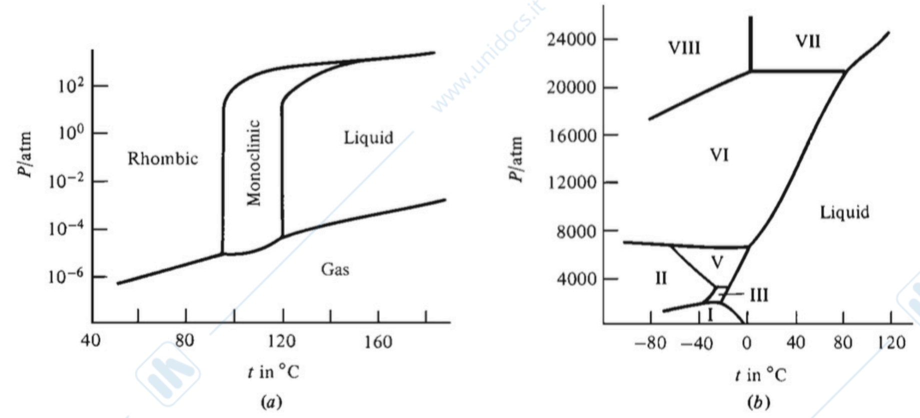


Figure 7.9

(*a*) Part of the sulfur phase diagram. The vertical scale is logarithmic. (Orthorhombic sulfur is commonly, but inaccurately, called rhombic sulfur.) (*b*) A portion of the H_2O phase diagram at high pressure.

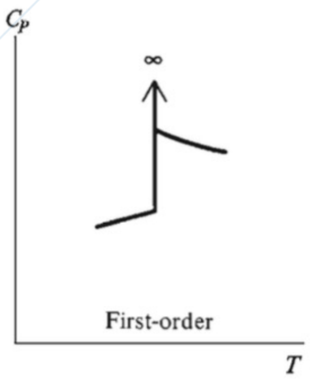
Ordine di transizione

Transizione del I ordine

li

Elevata variazione
di volume nella Transizione

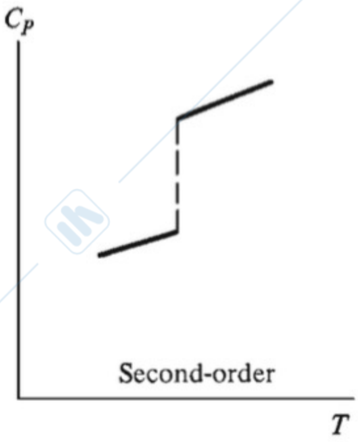
$\Delta H \neq 0$



(a)

Transizioni di ordine superiore

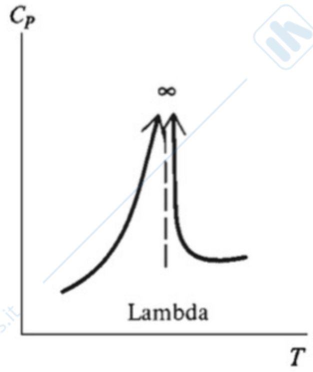
$q_p = \Delta H = T\Delta S = 0 \; ; \; \Delta V = 0$



Nelle Transizione di ordine superiore l'equazione di Clausius-Clapeyron non ha significato.

Nelle Transizioni del secondo ordine cp varia di una quantità finita

Transizioni lambda



$\Delta H = T\Delta S = 0 = \Delta V$

al punto λ la temperatura T_λ e Cp

1) $C_p \to \infty$ quando la Temperatura diminuisce raggiungendo T_λ

2) C_p cresce quando la Temperatura aumenta raggiungendo T_λ

Regione all'interfase