

Thermodynamics & Statistical Physics

Chapter 4. Multi-component multi-phase system

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 $S = \sum_i n_i s_i$; also $G = \sum_i n_i \mu_i$.
- Naturally, $v_i = \left(\frac{\partial V}{\partial n_i} \right)_{T, p, n_{j(j \neq i)}}$, $u_i = \left(\frac{\partial U}{\partial n_i} \right)_{T, p, n_{j(j \neq i)}}$,
 $s_i = \left(\frac{\partial S}{\partial n_i} \right)_{T, p, n_{j(j \neq i)}}$, $\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_{j(j \neq i)}}$.

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- For multi-component multi-phase system, phase α :

$$dU^\alpha = T^\alpha dS^\alpha - p^\alpha dV^\alpha + \sum_i \mu_i^\alpha dn_i^\alpha,$$

$$dG^\alpha = -S^\alpha dT^\alpha + V^\alpha dp^\alpha + \sum_i \mu_i^\alpha dn_i^\alpha,$$

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For G , as $G^{\alpha} = U^{\alpha} - T^{\alpha} S^{\alpha} + p^{\alpha} V^{\alpha}$, only if
 $p^{\alpha} = p^{\beta} = \dots$, and $T^{\alpha} = T^{\beta} = \dots$, $G = \sum_{\alpha} G^{\alpha}$.

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 $\Rightarrow \mu_i^\alpha = \mu_i^\beta$, equilibrium condition.

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- For single-component system: one phase, (T, p) , two independent; two phases coexist, Clapeyron equation, one independent; three phases coexist, one point.
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- Set $x_i^\alpha \equiv \frac{n_i^\alpha}{n^\alpha}$, intense parameter. As $\sum_i x_i^\alpha = 1$, only $k + 1$ independents. For φ phases, $(k + 1)\varphi$ independent intense parameters.

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vapour coexist, $k = 1, \varphi = 3, f = 0$.

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- In chemical equilibrium, suppose a virtual transition δn_i , then $\delta n_i = \nu_i \delta n$, where δn is the only independent variable.
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- $\Rightarrow \sum_i \nu_i \mu_i = 0$, condition of chemical equilibrium.
- If not, the process goes toward $\delta n \sum_i \nu_i \mu_i < 0$, except, any $\nu_i = 0$.

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$$\mu_i = \int c_{pi} dT - T \int c_{pi} \frac{dT}{T} + RT \ln(x_i p) + h_{i0} - T s_{i0}.$$
(2.4.13)

- Possible to write $G, H, U \dots$ (4.6.9,11,12,13).

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 $\therefore C$ is the entropy increase for the mixing. $C > 0$.
- If the two mixed gases are very close, transits to mix the same gas, there is a jump C for the entropy change, called **Gibbs paradox**.

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- A chemical reaction: $\sum_i \nu_i A_i = 0$, the condition for equilibrium: $\sum_i \nu_i \mu_i = 0$.
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Or using $p_i = x_i p$, $\prod_i x_i^{\nu_i} = p^{-\sum_i \nu_i} K_p$.

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- $\Rightarrow \varepsilon = \sqrt{\frac{1}{1 + bpT^{-\frac{5}{2}} e^{\frac{\Delta h_0}{RT}}}}$, where b is a constant, called
Saha equation. Determine the fraction of ionization for a given T and p .

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 - 4.7 Chemical equilibrium of ideal gas
 - 4.8 Third law of thermodynamics

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 If $\frac{\partial \Delta H}{\partial T} \Big|_{T=0} = \frac{\partial \Delta G}{\partial T} \Big|_{T=0}$, then $\lim_{T \rightarrow 0} (\Delta S)_T = 0$.
- The correctness of the 3rd law depends on the correctness of its inferences.

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$$\lim_{T \rightarrow 0} \beta = \lim_{T \rightarrow 0} \frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_V = 0. \text{ Proved by experiments.}$$

Inferences of the third law of thermodynamics and different expressions

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 3. Unattainability of $T = 0K$: impossible to cool to $T = 0K$ in a finite number of steps.

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