14.5: ∑μjdnj = 0 and Primitive Vs. Gibbsian Equilibrium

We conclude that $\sum_{j=1}^{\omega} \mu_j dn_j = 0$ is a criterion for reversible change in any system. When the change involves equilibria among two or more phases or substances, it alters the number of moles of the components present. An extent of reaction, $\xi = \left(n_j - n_j^o\right)/\nu_j$, characterizes the displacement of every such equilibrium. The magnitude of each incremental equilibrium displacement is specified by composition changes, $dn_j = \nu_j d\xi$, and conversely. The criterion for reversible change becomes $\sum_{j=1}^{\omega} \mu_j \nu_j d\xi = 0$. When this criterion is satisfied because $\sum_{j=1}^{\omega} \mu_j \nu_j = 0$, $d\xi$ is arbitrary, and the system can reversibly traverse a range of equilibrium states. In other words, $\sum_{j=1}^{\omega} \mu_j \nu_j = 0$ defines a Gibbsian equilibrium manifold.

We can also have a reversible process for which $d\xi = 0$. If the process is reversible, the state of the system corresponds to a point on the Gibbsian manifold, but $d\xi = 0$ stipulates that the system cannot change: it must remain at the specified point on the manifold. This corresponds to what we are calling a primitive equilibrium state. The system is constrained to remain in this state by the nature of its interactions with its surroundings: the system may be isolated, or the surroundings may act to maintain the system in a fixed state.

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