

14.2: Dependence of Other Thermodynamic Functions on the Composition

Using the appropriate sets of independent variables, we can obtain similar expressions for dH , dA , dG , and dS under the conditions that we assume in Section 14.1. Since entropy and pressure are the natural variables for enthalpy in a closed system, we infer that a change in the enthalpy of any system can be expressed as a function of dS , dP , changes in the non-pressure–volume work variables, $d\theta_k$, and changes in the composition, dn_j . That is, from

$$H = H(S, P, \theta_1, \theta_2, \dots, \theta_\lambda, n_1, n_2, \dots, n_\omega)$$

we have

$$\begin{aligned} dH = & \left(\frac{\partial H}{\partial S} \right)_{P, \theta_m, n_j} dS + \left(\frac{\partial H}{\partial P} \right)_{S, \theta_m, n_j} dP \\ & + \sum_{k=1}^{\lambda} \left(\frac{\partial H}{\partial \theta_k} \right)_{S, P, \theta_{m \neq k}, n_j} d\theta_k \\ & + \sum_{j=1}^{\omega} \left(\frac{\partial H}{\partial n_j} \right)_{S, P, \theta_m, n_{p \neq j}} dn_j \end{aligned}$$

From $H = E + PV$, we have

$$dH = dE + PdV + VdP$$

for any system. Substituting our result from [Section 14.1](#).

$$dE = TdS - PdV + dw_{NPV} + \sum_{j=1}^{\omega} \mu_j dn_j$$

where

$$\mu_j = \left(\frac{\partial E}{\partial n_j} \right)_{S, V, \theta_m, n_{p \neq j}}$$

we have

$$dH = TdS + VdP + dw_{NPV} + \sum_{j=1}^{\omega} \mu_j dn_j$$

Since we assume that both of these equations for dH describe open systems, all of the variables are independent, and the corresponding coefficients must be equal. For systems that satisfy our assumptions, we have

$$T = \left(\frac{\partial H}{\partial S} \right)_{P, \theta_m, n_j}$$

$$V = \left(\frac{\partial H}{\partial P} \right)_{S, \theta_m, n_j}$$

$$dw_{NPV} = \sum_{k=1}^{\lambda} \left(\frac{\partial H}{\partial \theta_k} \right)_{S, V, \theta_{m \neq k}, n_j} d\theta_k$$

and

$$\mu_j = \left(\frac{\partial H}{\partial n_j} \right)_{S, P, \theta_m, n_{p \neq j}} = \left(\frac{\partial E}{\partial n_j} \right)_{S, V, \theta_m, n_{p \neq j}}$$

By parallel arguments, we find

$$dA = -SdT - PdV + dw_{NPV} + \sum_{j=1}^{\omega} \mu_j dn_j$$

with

$$\mu_j = \left(\frac{\partial A}{\partial n_j} \right)_{T, V, \theta_m, n_{p \neq j}}$$

and

$$dG = -SdT + VdP + dw_{NPV} + \sum_{j=1}^{\omega} \mu_j dn_j$$

with

$$\mu_j = \left(\frac{\partial G}{\partial n_j} \right)_{T, P, \theta_m, n_{p \neq j}}$$

Rearranging the result for dE , we find

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{dw_{NPV}}{T} - \frac{1}{T} \sum_{j=1}^{\omega} \mu_j dn_j$$

so that

$$\mu_j = -T \left(\frac{\partial S}{\partial n_j} \right)_{E, V, \theta_m, n_{p \neq j}}$$

and from the result for dH , we have

$$dS = \frac{1}{T}dH - \frac{V}{T}dP - \frac{dw_{NPV}}{T} - \frac{1}{T} \sum_{j=1}^{\omega} \mu_j dn_j$$

so that

$$\mu_j = -T \left(\frac{\partial S}{\partial n_j} \right)_{H, P, \theta_m, n_{p \neq j}}$$

Evidently, for any system whose condition corresponds to our assumptions, all of the relationships that we develop in [Section 10.1](#) remain valid. The non-pressure–volume work can be expressed in terms of partial derivatives in several equivalent ways:

$$\begin{aligned} dw_{NPV} &= \sum_{k=1}^{\lambda} \left(\frac{\partial E}{\partial \theta_k} \right)_{S, V, \theta_{m \neq k}, n_j} d\theta_k \\ &= \sum_{k=1}^{\lambda} \left(\frac{\partial H}{\partial \theta_k} \right)_{S, P, \theta_{m \neq k}, n_j} d\theta_k \\ &= \sum_{k=1}^{\lambda} \left(\frac{\partial A}{\partial \theta_k} \right)_{V, T, \theta_{m \neq k}, n_j} d\theta_k \\ &= \sum_{k=1}^{\lambda} \left(\frac{\partial G}{\partial \theta_k} \right)_{P, T, \theta_{m \neq k}, n_j} d\theta_k \\ &= -T \sum_{k=1}^{\lambda} \left(\frac{\partial S}{\partial \theta_k} \right)_{E, V, \theta_{m \neq k}, n_j} d\theta_k \\ &= -T \sum_{k=1}^{\lambda} \left(\frac{\partial S}{\partial \theta_k} \right)_{H, P, \theta_{m \neq k}, n_j} d\theta_k \end{aligned}$$

Most importantly, the chemical potential and the criteria for change can be expressed in several alternative ways. We have

$$\begin{aligned}\mu_j &= \left(\frac{\partial E}{\partial n_j} \right)_{S, V, \theta_m, n_{p \neq j}} = \left(\frac{\partial H}{\partial n_j} \right)_{S, P, \theta_m, n_{p \neq j}} \\ &= \left(\frac{\partial A}{\partial n_j} \right)_{V, T, \theta_m, n_{p \neq j}} = \left(\frac{\partial G}{\partial n_j} \right)_{P, T, \theta_m, n_{p \neq j}} \\ &= -T \left(\frac{\partial S}{\partial n_j} \right)_{E, V, \theta_m, n_{p \neq j}} = -T \left(\frac{\partial S}{\partial n_j} \right)_{H, P, \theta_m, n_{p \neq j}}\end{aligned}$$

For any system, open or closed, that satisfies the assumptions we introduce in §1, the criteria for change are

$$\sum_{j=1}^{\omega} \mu_j dn_j \leq 0$$

where the chemical potential is equivalently expressed as any of the partial derivatives above.

Let us review the scope and significance of these results. We develop the fundamental equation, $dE = TdS - PdV + dw_{NPV}$, by reasoning about the behavior of closed, reversible systems. For any process in a closed system, we develop the criteria for change

$$(\Delta E)_{SV} \leq w_{NPV}$$

$$(\Delta H)_{SP} \leq w_{NPV}$$

$$(\Delta A)_{VT} \leq w_{NPV}$$

$$(\Delta G)_{PT} \leq w_{NPV}$$

$$(\Delta S)_{EV} \geq -w_{NPV}/\hat{T}$$

$$(\Delta S)_{HP} \geq -w_{NPV}/\hat{T}$$

and the corresponding relationships among differentials for incremental changes. Now we are extending these conclusions to produce equations for the changes in the various thermodynamic functions when a system undergoes a spontaneous composition change. To do so, we introduce the idea that composition variables must be included in a complete model for a thermodynamic function. When we write

$$E = E(S, V, \theta_1, \theta_2, \dots, \theta_\lambda, n_1, n_2, \dots, n_\omega)$$

we assert that every set of values, $\{S, V, \theta_1, \theta_2, \dots, \theta_\lambda, n_1, n_2, \dots, n_\omega\}$, corresponds to a state of the system in which the system has a definite energy. (Of course, we are not asserting that every such set of values can actually be attained by the real system. Many such sets correspond to hypothetical states. The particular sets of values that do correspond to realizable states of the system lie on a manifold. Given one such set of values—one point on the manifold—our differential expressions specify all of the other states that lie on the same manifold.)

When we assume that the various partial derivatives, $(\partial E/\partial S)_{V, \theta_k, n_j}$, $(\partial E/\partial V)_{S, \theta_k, n_j}$, $(\partial E/\partial \theta_k)_{S, V, \theta_{m \neq k}, n_j}$, and $(\partial E/\partial n_j)_{S, V, \theta_k, n_{p \neq j}}$, exist, we are assuming that E is a smooth, continuous function of each of these variables. Since some of these partial derivatives are synonymous with intensive variables, we are assuming that these intensive variables are well defined. Moreover, since these intensive variables characterize the system as a whole, we are assuming that each intensive variable has the same value in every part of the system¹. When we assume that $\mu_j = (\partial E/\partial n_j)_{S, V, \theta_m, n_{p \neq j}}$ has a well-defined value, we are assuming that E is a continuous function of n_j ; we are assuming that μ_j exists for any arbitrary state of the system and not just for states undergoing reversible change.

When we assume that an arbitrary change is described by the total differential $dE = TdS - PdV + dw_{NPV} + \sum_{j=1}^{\omega} \mu_j dn_j$, we are going beyond our conclusion that this total differential describes paths of reversible change. We are asserting that it describes any process in which a change in composition is the sole source of irreversibility. As a practical matter, we expect it to describe any process that occurs in a system whose potential functions are well defined. By well defined, we mean, of course, that they can be measured and that the measurements are reproducible and consistent. We expect these conclusions to apply to multiple-phase, open systems, so long as each potential has the same value in every phase. In thus assuming that we can expand the scope of the fundamental equation, we are not modifying the change criteria that we develop in [Chapter 9](#). Our conclusions that $(dE)_{SV} = dw_{NPV}$ for a reversible process and $(dE)_{SV} < dw_{NPV}$ for a spontaneous process in a closed system are not affected.

Again, while our arguments for them are compelling, these results are not rigorously logical consequences of our earlier conclusions about reversible processes. As for any scientific principle, their validity depends on their predictive capability, not their provenance.

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