

Review of General Relations

1. The goal: investigate the evolution of thermodynamic properties (E, S, P, T, V) as functions of two independent variables (such as T and V, or T and P, or P and V, depending on what are required).
2. The approach: the key step is to find the inter-relation between thermodynamic properties in differential forms. For example, to find a property F as a function of two independent variables x and y, we write the differential form as $dF = \frac{\partial F}{\partial x} \Big|_y dx + \frac{\partial F}{\partial y} \Big|_x dy$.

The ways to find the partial derivatives include:

- a. From thermodynamic laws. For example, from $dE = TdS - PdV$, we get: $\frac{\partial E}{\partial S} \Big|_V = T$, $\frac{\partial E}{\partial V} \Big|_S = -P$. For another example, by re-writing the first law as $dS = \frac{1}{T} dE + \frac{P}{T} dV$, we get $\frac{\partial S}{\partial E} \Big|_V = \frac{1}{T}$, $\frac{\partial S}{\partial V} \Big|_E = \frac{P}{T}$.

- b. From mathematical properties of exact differentials. Note that the differentials of thermodynamic state variables (E, S, P, V, T) and their combinations (e.g. thermodynamic potentials H, F, G) are exact differentials. These mathematical properties are summaries as the Maxwell relations (Stowe Table 9.3). It should be noted that the Maxwell relations give partial derivatives between P, V, S, and T. In many circumstances, the P-V-T relation can be derived from the equation of state (see c below), which is often given. So it is often convenient to utilize the partial derivatives of S with respect to T or V or P. In this way, we may first find dS , and then use the first law to find dE .

- c. Differentiating the equation of state of a specific system. For example, for an ideal gas: $PV = nRT$; in differential form: $PdV + VdP = RdT$. For another example, for a Van der Waals gas: $\left(P + \frac{a}{v^2}\right)(v-b) = RT$; in differential form:

$$(v-b)dP + \left[P + \frac{a}{v^2} - \frac{2a(v-b)}{v^3} \right] dv = RdT .$$

- d. Making use of properties measured or tabulated in laboratories, including:

$$\text{heat capacities : } C_V = \frac{T\partial S}{\partial T} \Big|_V, C_P = \frac{T\partial S}{\partial T} \Big|_P$$

$$\text{volume expansion coefficient : } \beta = \frac{1}{V} \frac{\partial V}{\partial T} \Big|_P$$

$$\text{isothermal compressibility : } \kappa_T = -\frac{1}{V} \frac{\partial V}{\partial P} \Big|_T$$

$$\text{adiabatic compressibility : } \kappa_S = -\frac{1}{V} \frac{\partial V}{\partial P} \Big|_S$$

3. A specific constraint of the system helps to reduce the number of independent variables, or lead to the relation between two variables which are originally independent of each other when without the constraint. For example, if a system evolves adiabatically ($dS = 0$), then the relationship between dP and dT , which could be independent variables

without the $dS=0$ constraint, can be derived by $dS = \left. \frac{\partial S}{\partial T} \right|_P dT + \left. \frac{\partial S}{\partial P} \right|_T dP = 0$, or

$$\left. \frac{\partial P}{\partial T} \right|_S = - \frac{\left. \frac{\partial S}{\partial T} \right|_P}{\left. \frac{\partial S}{\partial P} \right|_T}.$$

- Note that the above approaches can be applied to a general thermodynamic system other than a gas, for which the first law is written as $dE = TdS - FdX$. Here, F is the generalized force, which replaces the gas pressure P in all above relations, X is the external variable or displacement under the generalized force F , and X should replace V in all above relations. For example, for a stretched rubber band is a thermodynamic system, its tension force is the generalized force, and its length is the generalized external variable or displacement. For another example, for a soap bubble, the surface tension force is the generalized force, and the surface area of the bubble is the generalized displacement. Note that when writing the expression of dW , make sure that by definition, dW is the work done by the system against an external force (such as an external force pulling the stretched rubber band or soap bubble, or an external pressure force compressing a gas).