

Part II: Thermodynamics

II.5 Application: General Relations

Class schedule: Feb 24, 26

Reading assignments: S9-10, R5.5-5.8, F16-18

Examples marked with * are important and should be studied carefully.

Review: in thermodynamics, we often need study the differential relationship between macroscopic thermodynamic properties ($E, S, T, P, V, C_p, \beta, \kappa \dots$) from thermodynamic laws (the first and second laws) with given models (such as equations of state for gases, liquids, or solids) and constraints (such as an isobaric, isothermal, adiabatic process). The practical reason is that in various circumstances certain properties can be measured or controlled in laboratories, and the other properties should then be derived from these differential relations.

*Example 1: review thermodynamic properties of an ideal gas; note the switch between dependent and independent variables when deriving these properties.

II.5.1 Van Der Waals Gas

Real gas: a gas can be compressed into a limiting volume - the volume of liquid state, and particle interaction can no longer be ignored, and the equation of state deviates from the ideal gas law. The real gas is described by the *van der Waals equation of state*:

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

Remark 1: note that v in the equation is the molar volume $v = V/n$.

Remark 2: for a dilute gas at not very low temperature, $a \sim 0, b \sim 0$, the Van Der Waals equation is reduced to the ideal gas law.

Example 2: intermolecular forces and the “touch-on” distance between gas particles

*Example 3: thermodynamic properties (specific heats, internal energy, entropy, and adiabatic process) of a real gas (Fermi 16)

Note that, unlike an ideal gas, for a real gas, the internal energy is a function of both temperature and volume. Taking T and V as independent variables, it can be generally written

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV$$

The partial derivatives in the equation can be experimentally measured (such as heat capacities), or determined by the inter-relationship between macroscopic properties derived from thermodynamic laws and equations of state. For example,

$$\frac{\partial E}{\partial V} = T \left(\frac{\partial P}{\partial T}\right)_V - P$$

The same inter-relationship can be determined in general systems with generalized work, other than work done by pressure, such as in a stretched wire, surfaces, electrochemical cell (see Reif Problems 5.14, 5.15, 5.16). All these systems can be treated as thermodynamic systems.

II.5.2 Thermodynamic Potentials and Maxwell Relations

Thermodynamic properties are inter-related by *Maxwell relations*, a set of partial derivatives with respect to different independent variables. In non-diffusive systems ($dN = 0$), we have seen that only two independent variables are necessary to describe all other properties. The basis of Maxwell relations is:

- thermodynamic laws, or $TdS = dE + PdV$ (note: in general form, PdV is replaced by $\Sigma_{\alpha}F_{\alpha}d\alpha$)
- mathematical properties of state variables, or the fact that differentials of many thermodynamic variables are exact differentials. Given $dF = A(x, y)dx + B(x, y)dy$ being an exact differential, there must be $\partial A/\partial y)_x = \partial B/\partial x)_y$.

For example, using above, we found the general expression for $\partial E/\partial V)_T$.

Example 4: calculate E and S from experimental measurables.

Remark: E and S can be calculated from experimentally measured specific heats and the equation of state, aided by Maxwell relations.

To generalize such, some *thermodynamic potentials* like the internal energy are introduced, and will be studied in given systems/circumstances.

a. Internal energy E : $dE = TdS - PdV$, saying that E is determined by independent variables S and V . By writing $dE = \partial E/\partial S)_V dS + \partial E/\partial V)_S dV$, it is seen that $\partial E/\partial S)_V = T$, and $\partial E/\partial V)_S = -P$. The resultant Maxwell relation is: $\partial T/\partial V)_S = -\partial P/\partial S)_V$.

b. Helmholtz free energy $F \equiv E - TS$, $dF = -PdV - SdT$. Importantly, if a system is in constant contact with the environment or a heat reservoir to maintain a constant temperature, in such an isothermal process, the amount of work done is the decrease of Helmholtz free energy. For this reason, F is sometimes called "work function". In an isothermal and dynamically insulated process, F is conserved.

Example 5: calculate F for an ideal gas and a real gas

c. Enthalpy $H \equiv E + PV$, $dH = TdS + VdP$. In an isobaric process, $dH = TdS = dQ$, so H is sometimes called "heat function". In a adiabatic and isobaric process, or a throttling process, H is conserved.

d. Gibbs free energy $G \equiv E - TS + PV$, $dG = -SdT + VdP$. G is examined when studying phase transition.

*Example 6: application of Maxwell relations (Reif Prob. 5.12)

Remark: one can always write the expression of a dependent variable dF as a function of chosen independent variables dx and dy in the form of $dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy$, and use general (Maxwell relation) and specific properties, or laboratory measured relations/quantities of the thermodynamic system to find out the partial derivatives.