General Physics II: Tutorial Material

Lecture 11 (Chapter 10, Thermodynamic potentials)

1) Fundamental relations for specific quantities: It is common practice, in particular in chemistry, to use state functions that are specific quantities, i.e. extensive quantities per unit of volume or mass. Let's consider a simple system that has an internal energy $E_{int}(S, V, n_i)$. The volume densities e, s, ν_i are defined as

$$e = \frac{E_{int}}{V}, \quad s = \frac{S}{V}, \quad \nu_i = \frac{n_i}{V} \tag{1}$$

The mass densities e^*, s^*, ν^* are defined as

$$e^* = \frac{E_{int}}{M}, \quad s^* = \frac{S}{M}, \quad \nu_i^* = \frac{V}{M} \tag{2}$$

The mass chemical potential μ_i^* and the mass concentration c_i^* of substance i are defined as

$$\mu_i^* = \frac{\mu_i}{M_i^*}, \quad c_i^* = \frac{n_i M_i^*}{M} \tag{3}$$

with M_i^* being the molar mass of substance i.

Determine the Gibbs, Euler and Gibbs-Duhem relations expressed in terms of e, s, ν_i.

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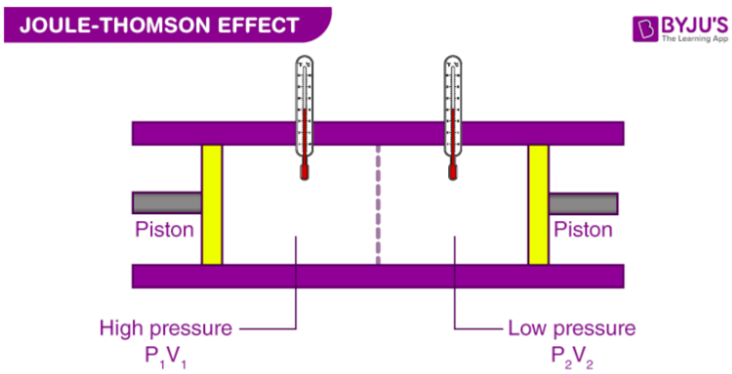
2) Joule-Thomson Expansion: Consider a Cylinder closed by two sliding pistons separated by a permeable fixed wall. The cylinder contains n moles of an ideal gas passing through the wall under the effect of pistons 1 and 2 that keep the pressures P_1 and P_2 constant in the subsystems 1 and 2 on both sides of the wall. The device is an adiabatic closed system.



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a) Show that the enthalpy H is conserved if the external pressures exerted by the pistons are equal to the pressures in the corresponding subsystems at all times, i.e. $P_{1,ext} = P_1$ and $P_{2,ext} = P_2$. This is called the Joule Thomson expansion.

b) For an arbitrary gas and an infinitesimal pressure different dP, show that the Joule Thomson coefficient, defined as the partial derivative of temperature T with respect to the pressure P, is given by:

$$\frac{\partial T}{\partial P} = \frac{(T\alpha - 1)V}{c_P} \tag{4}$$

Where α is the thermal expansion coefficient defined as:

$$\alpha = \frac{1}{V}\frac{\partial V}{\partial T} \tag{5}$$

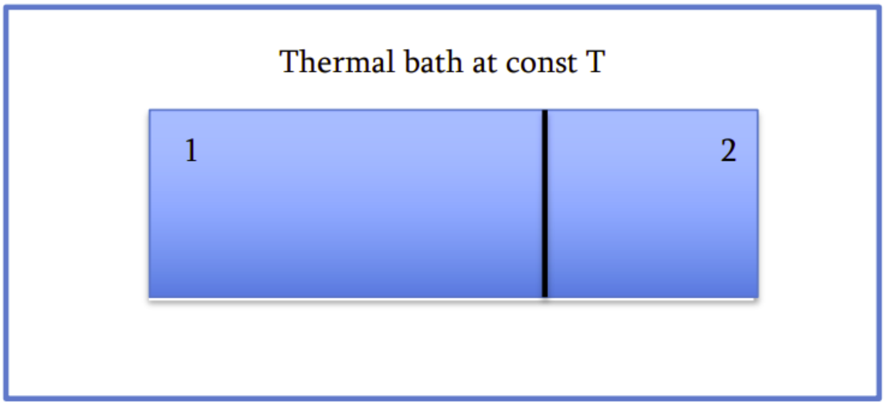
And c_P the specific heat at constant pressure defined as:

$$c_P = \frac{\partial H}{\partial T}\Big|_P = T\frac{\partial S}{\partial T} \tag{6}$$

3) Simple subsystems in a thermal bath: We consider a rigid, (i.e., V constant) closed system containing a homogeneous gas. The system is divided in two simple subsystems that are separated by a moveable, impermeable diathermal wall. The system is in thermal equilibrium with a thermal bath at temperature $T = const$. The kinetic and internal energies of the wall are negligible.

a) Express the differential of the free energy dF as a function of the infinitesimal heat dQ provided to the system.

b) Express the differential of the free energy dF as a function of the pressures P_1 and P_2 of the gas in the subsystems 1 and 2. Deduce that $dF \leq 0$.



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4) Adiabatic compression: An ideal gas is characterized by the enthalpy $H(S, P) = C_P T$, where C_P is a constant (the heat capacity at constant pressure). An adiabatic reversible compression brings the pressure from P_1 to P_2 where $P_2 > P_1$. The initial temperature is T_1. Determine the temperature T_2 at the end of the compression.

5) Grand potential: The **Grand potential** $\Phi(T, V, \mu)$, also known as the Landau free energy, is a thermodynamical potential obtained by performing the Legendre transformations of the internal energy $E_{int}(S, V, n)$ with respect to S and n. Use Legendre transformations to express the thermodynamical potential $\Phi(T, V, \mu)$ in terms of the thermodynamical potential F. Also determine the differential $d\Phi(T, V, \mu)$.