

## Appendix A: Derivation of the chemical potential equation

The expression that is commonly used in planetary atmospheres is usually written as (*Kodepudi and Prigogine [1998]*, Eq. 5.3.6):

$$\mu(p, T) = \mu(p_0, T) + RT \ln(p/p_0) \quad (\text{A1})$$

where  $\mu_0$  is the chemical potential at unit pressure (1 atm),  $p_0$  is the pressure at standard conditions and R the gas constant.

In order to calculate the chemical potential for arbitrary p and T, the knowledge of the chemical potential at  $(p_0, T)$  is needed. This previous step, usually omitted, can be performed as (Eq. (5.3.3) in (*Kodepudi and Prigogine [1998]*)):

$$\mu(p_0, T) = \frac{T}{T_0} \mu(p_0, T_0) + T \cdot \int_{T_0}^T \frac{-H_m(p_0, T')}{T'^2} dT' \quad (\text{A2})$$

where  $T_0$  is the temperature at standard conditions and  $H_m$  is the molar enthalpy of the compound.

Therefore, the most complete equation to determine the chemical potential for a compound at a particular pressure and temperature is the expression:

$$\mu(p, T) = \frac{T}{T_0} \mu(p_0, T_0) + T \cdot \int_{T_0}^T \frac{-H_m(p_0, T')}{T'^2} dT' + RT \ln(p/p_0) \quad (\text{A3})$$

The molar enthalpy  $H_m(p_0, T)$  at an arbitrary temperature T can be obtained from the values of the heat capacity at constant pressure,  $C_p(T)$ , and the tabulated values of enthalpy at a standard temperature  $H(p_0, T_0)$ :

$$H_m(p_0, T) = H_m(p_0, T_0) + \int_{T_0}^T C_p(T) dT \quad (\text{A4})$$

Using this last relation, the enthalpy integral can be simplified to:

$$\int_{T_0}^T \frac{-H_m(p_0, T')}{T'^2} dT' = - \int_{T_0}^T \frac{H_m(p_0, T_0) + \int_{T_0}^{T'} C_p(T'') dT''}{T'^2} dT' \quad (\text{A5})$$

For the case of Mars, we can consider the heat capacity as a constant,  $C_p = C_p(T)$ , being able to extract it from the integral and obtaining (see the discussion for hot exoplanets later):

$$\begin{aligned} & - \int_{T_0}^T \frac{H_m(p_0, T_0) + C_p(T' - T_0)}{T'^2} dT' = \\ & - \int_{T_0}^T \frac{H_m(p_0, T_0) - C_p T_0 + C_p T'}{T'^2} dT' = \\ & -(H_m(p_0, T_0) - C_p T_0) \int_{T_0}^T \frac{1}{T'^2} dT' - C_p \int_{T_0}^T \frac{1}{T'} dT' = \\ & +(H_m(p_0, T_0) - C_p T_0) \left[ \frac{1}{T} - \frac{1}{T_0} \right] - C_p \ln \frac{T}{T_0} \quad (\text{A6}) \end{aligned}$$

Using (A6) and (A3), we obtain a useful approximation for the calculation of the chemical potential at the Martian environment

$$\mu(p, T) = \frac{T}{T_0} \mu(p_0, T_0) + T \cdot (H_m(p_0, T_0) - C_p T_0) \left[ \frac{1}{T} - \frac{1}{T_0} \right]$$

$$-C_p T \ln\left(\frac{T}{T_0}\right) + RT \ln(p/p_0) \quad (\text{A7})$$

When the temperature is  $T=T_0$ , the above expression is reduced to the more familiar equation:

$$\mu(p, T_0) = \mu(p_0, T_0) + RT_0 \ln(p/p_0) \quad (\text{A8})$$

However, as has been explained in Section 2, this expression is only useful for situations where the temperature is close to the standard temperature of reference (usually 298 K), i.e., the Earth environment. When the temperatures are different, the complete expression for the chemical potential is needed.

The temperature dependence of the heat capacity is usually expressed as a polynomial function with tabulated constants:

$$C_p(T) = a + bT + cT^2 \quad (\text{A9})$$

If the coefficients b and c are much smaller than a, as usually happens, Equation A7 represents an useful approximation, useful for those environments where the temperature variations are not large and the heat capacity can be considered as constant. For Venus and hot exoplanets a more detailed expression might be needed.

The molar enthalpy at an arbitrary temperature reads now:

$$H(p_0, T) = H(p_0, T_0) + \int_{T_0}^T a + bT + cT^2 dT$$

$$H(p_0, T) = H(p_0, T_0) - (aT_0 + \frac{b}{2}T_0^2 + \frac{c}{3}T_0^3) + (aT' + \frac{b}{2}T'^2 + \frac{c}{3}T'^3) \quad (\text{A10})$$

The enthalpy integral in Eq. A3 becomes:

$$\begin{aligned} & \int_{T_0}^T \frac{-H_m(p_0, T')}{T'^2} dT' = \\ & - \left( H(p_0, T_0) - (aT_0 + \frac{b}{2}T_0^2 + \frac{c}{3}T_0^3) \right) \int_{T_0}^T \frac{1}{T'^2} dT' \\ & - \int_{T_0}^T \frac{(aT' + \frac{b}{2}T'^2 + \frac{c}{3}T'^3)}{T'^2} dT' = \\ & + \left( H(p_0, T_0) - (aT_0 + \frac{b}{2}T_0^2 + \frac{c}{3}T_0^3) \right) \left[ \frac{1}{T} - \frac{1}{T_0} \right] \\ & - a \ln \left( \frac{T}{T_0} \right) - \frac{b}{2}(T - T_0) - \frac{c}{6}(T^2 - T_0^2) \quad (\text{A11}) \end{aligned}$$

Note that when we consider the coefficients b and c = zero, i.e.,  $C_p$  is not temperature dependent, then  $C_p = a$  and the expression A11 is reduced to A6.

We can use A11 into the chemical potential formula detailed in A3 and obtain a general equation for the chemical potential for an arbitrary pressure and temperature, useful for any planetary atmosphere:

$$\mu(p, T) = \frac{T}{T_0} \mu(p_0, T_0) + T \cdot \int_{T_0}^T \frac{-H_m(p_0, T')}{T'^2} dT' + RT \ln(p/p_0)$$

$$\begin{aligned} \mu(p, T) = & \frac{T}{T_0} \mu(p_0, T_0) + RT \ln(p/p_0) + \\ & - T \left( H(p_0, T_0) - (aT_0 + \frac{b}{2}T_0^2 + \frac{c}{3}T_0^3) \right) \left[ \frac{1}{T} - \frac{1}{T_0} \right] \\ & - aT \ln \left( \frac{T}{T_0} \right) - \frac{b}{2}T(T - T_0) - \frac{c}{6}T(T^2 - T_0^2) \quad (\text{A12}) \end{aligned}$$

Although these equations have been obtained by direct integration of the chemical potential equation, it is important to remark that it is possible to obtain the same equations by Legendre transformations. By definition, the Gibbs potential function is given as:

$$G = H - TS \quad (\text{A13})$$

The G function is called chemical potential in the case of one mol, and including the proper dependence of pressure and temperature in the equation, we can write:

$$\mu(p, T) = h(p, T) - T \cdot s(p, T) \quad (\text{A14})$$

The determination of the enthalpy and entropy at different (p,T) can be done using:

$$h(p, T) = h(p_0, T_0) + \left[ \int_{T_0}^T C_p dT \right]_{p_0} + \left[ \int_{p_0}^p -\mu_{JT} C_p dp \right]_T$$

$$s(p_0, T) = s(p_0, T_0) + \left[ \int_{T_0}^T \frac{C_p}{T} dT \right]_{p_0} - \left[ \int_{p_0}^p \left( \frac{\partial V}{\partial T} \right)_p dp \right]_T$$

where  $\mu_{JT}$  is the Joule-Thompson coefficient

$$\mu_{JT} = \left( \frac{\partial T}{\partial P} \right)_H = \frac{V}{C_p} (\alpha T - 1)$$

and  $\alpha$  is the volumetric thermal expansion coefficient,  $\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$ ; for an ideal gas is easy to prove that  $\alpha = \frac{1}{T}$ , and therefore  $\mu_{JT} = 0$ .

If we consider the first step in Figure 1, i.e., the variation in temperature without any changes in the pressure, and knowing the enthalpy and entropy variations on temperature (considering  $C_p$  as constant):

$$\mu(p_0, T) = h(p_0, T_0) + C_p(T - T_0) - T \cdot s(p_0, T_0) - C_p T \ln\left(\frac{T}{T_0}\right) \quad (\text{A15})$$

We consider now the second step in Figure 1, the pressure variation. The Joule-Thompson coefficient is zero for an ideal gas and therefore the pressure term in the enthalpy becomes zero, being the pressure dependence due to the entropy expression. The final equation for the chemical potential reads:

$$\mu(p, T) = h(p_0, T_0) - T \cdot s(p_0, T_0) + C_p(T - T_0) - C_p T \ln\left(\frac{T}{T_0}\right) + RT \ln\left(\frac{p}{p_0}\right) \quad (\text{A16})$$

It is trivial to prove that Equation A8 and Equation A16 are in fact the same equation where  $\mu(p_0, T_0) = h(p_0, T_0) - T_0 \cdot s(p_0, T_0)$ .