EP 2827: Thermodynamics

Saha Equation for stellar atmospheres

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1 Short recap of material covered in class

Consider the following reversible chemical reaction,

$$\sum_l \nu_l X_l = 0. \tag{1}$$

Here the subscript l denotes the l-th chemical species, be it reactants or products, the X_l is the chemical symbols for the l-th chemical species and ν_l is the stoichiometric coefficient (or stoichiometric weight) of the l-th chemical species participating in the reaction with the convention that the products have $\nu_l > 0$ and the reactants have $\nu_l < 0$. For example consider the reaction,

$$2H_2 + O_2 \leftrightharpoons 2H_2O.$$

As per our convention we first rewrite the reaction by bringing over the reactants to the products side,

$$2H_2O - 2H_2 - O_2 = 0.$$

So here $l = 1, 2, 3$ because there are three chemical species participating in the reaction, namely H_2O, H_2 and O_2. We will take, $X_1 = H_2O$, $X_2 = H_2$ and $X_3 = O_2$. The stoichiometric weights are $\nu_1 = 2$, $\nu_2 = -2$, $\nu_3 = -1$.

Recall that in class we derived the ***law of mass action*** of physical chemistry applying thermodynamics for a system undergoing the reversible reaction (1) at a temperature T and under pressure P,

$$\prod_l (x_l)^{\nu_l} \, P^{\sum_l \nu_l} = K(T) \tag{2}$$

where $K(T)$ is purely a function of the temperature for a given reaction, traditionally called by chemists as the *equilibrium constant*. By applying thermodynamics and assuming that the reactants as well as products are ideal gases, we saw in class, that the equilibrium constant is given by,

$$\ln K(T) = -\sum_l \nu_l \, \phi_l(T) \tag{3}$$

where the function $\phi_l(T)$ is a term in the expression for the molar Gibbs potential of the l-th chemical species of an ideal gas defined by the equation,

$$\phi_l(T) = \frac{h_{0,l}}{RT} - \frac{1}{R}\int^T dT' \frac{\int^{T'} c_{P,l} dT''}{T'^2} - \frac{s_{0,l}}{R}.$$

Here h_0, s_0 are constants of integration which are related to the constants of integration molar enthalpy, entropy and c_P is the molar heat capacity at constant pressure. Plugging this in the previous equation we have the expression for the equilibrium constant under a chemical reaction as a function of temperature,

$$\begin{aligned}
\ln K(T) &= -\sum_l \nu_l \left(\frac{h_{0,l}}{RT} - \frac{1}{R}\int^T dT' \frac{\int^{T'} c_{P,l} dT''}{T'^2} - \frac{s_{0,l}}{R} \right) \\
&= -\frac{\left(\sum_l \nu_l h_{0,l}\right)}{RT} + \frac{1}{R}\int^T dT' \frac{\int^{T'} \left(\sum_l \nu_l c_{P,l}\right) dT''}{T'^2} + \frac{\left(\sum_l \nu_l s_{0,l}\right)}{R} \\
&= -\frac{\Delta h_0}{RT} + \frac{1}{R}\int^T dT' \frac{\int^{T'} \Delta c_P dT''}{T'^2} + \frac{\Delta s_0}{R}. \qquad (4)
\end{aligned}$$

This result is known as the ***Nernst equation***, which had been obtained experimentally by chemists. Taking a derivative with respect to the temperature of both sides, we get,

$$\begin{aligned}
\frac{d}{dT}\ln K(T) &= -\sum_l \nu_l \frac{d\phi_l(T)}{dT} \\
&= \sum_l \nu_l \left(\frac{h_{0,l}}{RT^2} + \frac{1}{R}\frac{\int^T c_{P.l} dT'}{T^2} \right) \\
&= \frac{\sum_l \nu_l \, h_l}{RT^2} \\
&= \frac{\Delta h}{RT^2},
\end{aligned}$$

where we have used the fact the molar enthalpy of the ideal gas is given by $h = h_0 + \int^T c_{P.l} dT'$ in going from the second to the third line and we have also defined $\Delta h = \sum_l \nu_l \, h_l$, the enthalpy change in the reaction. Now the first law implies,

$$\Delta Q = \Delta U + P\Delta V = \Delta H - V\Delta P$$

Thus under conditions of constant temperature and constant pressure,

$$\Delta Q = \Delta H,$$

or using molar amounts,

$$\Delta q = \Delta h$$

i.e. the heat absorbed (per mole) is equal to the change in (molar) enthalpy. Thus we have the beautiful equation,

$$\frac{d}{dT}\ln K(T) = \frac{\Delta h}{RT^2} = \frac{\Delta q_{reaction}}{RT^2}.$$

Again this has been observed by chemists long before it was derived theoretically. This equation is known as the ***van't Hoff isobar***.

2 Saha (ionization) equation

In 1920 M.N. Saha obtained a remarkable equation to predict the pressure of the outer atmosphere of distant star from the simple input of the spectrum of their emitted starlight. Since the stellar atmosphere temperatures are hot enough to ionize neutral constituents. Saha modeled the stellar atmosphere as made up of a monatomic ideal gas (call it gas A) where the following thermal ionization reaction is prevailing,

$$A \leftrightharpoons A^+ + e^-.$$

In our notation we rewrite the reaction as,

$$A^+ + e^- - A = 0.$$

Applying the law of mass action (2), one obtains

$$(x_{A^+})^1 \ (x_{e^-})^1 \ (x_A)^{-1} P^{1+1-1} = K(T)$$

or,

$$\ln K = \ln\left(\frac{x_{A^+}x_{e^-}}{x_A}P\right). \tag{5}$$

Now let ϵ be the *degree of reaction (ionization)* , and let's say there were n_0 moles of the unionized gas A to start with. Then in terms of ϵ and n_0, the current number of moles of the different species are given by,

$$\begin{aligned} n_A &= n_0(1-\epsilon), \\ n_{A^+} &= n_0\epsilon, \\ n_{e^-} &= n_0\epsilon, \end{aligned}$$

and total number of moles of everything is,

$$n = n_A + n_{A^+} + n_{e^-} = n_0(1+\epsilon).$$

Thus, the mole fractions are,

$$\begin{aligned} x_A &= \frac{n_A}{n} = \frac{1-\epsilon}{1+\epsilon}, \\ x_{A^+} &= \frac{n_{A^+}}{n} = \frac{\epsilon}{1+\epsilon}, \\ x_{e^-} &= \frac{n_{e^-}}{n} = \frac{\epsilon}{1+\epsilon}, \end{aligned}$$

Plugging these back in (5),

$$\ln K = \ln\left(\frac{\epsilon^2}{1-\epsilon^2}P\right) \tag{6}$$

Thus from the knowledge of $K(T)$, and the degree of ionization ϵ one can determine the pressure of the stellar atmosphere. The degree of ionization can be determined by ratio intensities of the light emitted from the ionized to that of unionized gas examining the emission spectrum of the starlight. How does one gain knowledge of K though? The answer is to apply the Nernst equation (4). For a monatomic gas we know from kinetic theory, $c_p = \frac{5R}{2}$. This means in this case,

$$\begin{aligned} \Delta c_p &= \nu_{A^+}c_{P,A^+} + \nu_{e^-}c_{P,e^-} + \nu_A c_{P,A} \\ &= \frac{5}{2}R, \end{aligned}$$

and the Nernst equation gives,

$$\ln K = -\frac{\Delta h_0}{RT} + \frac{5}{2}\ln T + \frac{\Delta s_0}{R}.$$

If the ionization energy of the reaction is E, then the molar heat of the reaction at zero temperature is, $\Delta h_0 = N_F E$. (At zero temperature from kinetic theory we are assuming the particles do not move i.e. have zero kinetic energy, hence the heat of the reaction is exactly equal to the ionization energy). Also from the Boltzmann postulate,

$$s = R\ln\Omega$$

where Ω is the number of internal molecular microstates. Applying this formula for each species in the ionization process,

$$\begin{aligned} \Delta s_0 &= \nu_{A^+}s_{0,A^+} + \nu_{e^-}s_{0,e^-} + \nu_A s_{0,A} \\ &= R\ln\frac{\Omega_{A^+}\Omega_{e^-}}{\Omega_A}. \end{aligned}$$

So the final form of the Nernst equation for this case is,

$$\ln K = -\frac{N_F E}{RT} + \frac{5}{2}\ln T + \ln\left(\frac{\Omega_{A^+}\Omega_{e^-}}{\Omega_A}\right).$$

Thus from the knowledge of the fundamental constants, the ionization energy, E, the atomic structure data i.e. Ω's and the temperature of the star from some other measurement (Wien's displacement law), one can determine the (log of) equilibrium constant. This completes the discussion of Saha's equation to determine the pressure of stellar atmospheres.