

## Review of some key relationships in representation of rate constants

(relevant to Chapters: 4N, 5N, 6N, 7N, HW 3 etc.)

### Rule 1.

The rate constant  $k$  for an elementary reaction can be represented by TST, as shown on the left hand side of the equation (1) below, or by the Arrhenius form, as shown on the right hand side.

$$\frac{k_B T}{h_p \gamma_z} e^{\frac{\Delta S^*}{R}} e^{-\frac{\Delta H^*}{RT}} = k_0 e^{-\frac{E}{RT}} \quad (1)$$

Clearly, the two sides have the same units, which are associated with the pre-exponential factors, and each has to be multiplied by the same reaction driving force to produce the same reaction rate. The key issue of guaranteeing not only the same rate but also the same sensitivity to temperature is taken care of by insisting that both the rate constant and its derivative with respect to temperature are the same at a selected temperature.

In terms of equation (1) this leads to the two requirements that:

$$E = \Delta H^* + RT \quad (2a)$$

$$k_0 = e \frac{k_B T}{h_p \gamma_z} e^{\frac{\Delta S^*}{R}} \quad (2b)$$

The natural logarithm base  $e$  appears in the pre-exponential factor, as shown by eq. (2b), to compensate for the use of  $E$  in the exponential term, which due to eq. (2a) contains now the  $e^{-1}$  term.

### Rule 2.

The rate for an  $n$ -th order reaction in appropriate desired units can be represented as

$$r = k_c C^n = k_p p^n \quad (3)$$

Species concentration and partial pressure are tied by an appropriate equation of state, for example ideal gas law

$$p = CRT \quad (4)$$

Using rule 1 above and eq. (4) lead to the following relationships between activation energies and pre-exponential factors of the two rate constants, as shown in the notes earlier:

$$E_c = E_p + nRT \quad (5a) \quad k_{c0} = e^n (RT)^n k_{p0} \quad (5b)$$

### Rule 3

The rate predicted by TST is the product of the universal frequency (1/s) and the concentration of the transition state. The fact that the transition state is in equilibrium with the reactants is represented by the thermodynamic equilibrium constant,  $K^*$ , which is unit-less. One must carefully use activity coefficients and pay attention to their units and definition of the standard state to find the final form of the rate expressed in terms of the reactant concentrations and/or partial pressures.