against $1/T$ is very difficult to detect, and any significant nonlinearity usually indicates that side-reactions are occurring!

Thermodynamics of the transition state

We shall see below (equation 2.5.15) that the high-pressure A-factor is related to $\Delta S^\ddagger$, the change in entropy on going from the reactant to the transition state in the following manner:

$$A_\infty = \frac{ek_BT}{h} e^{\Delta S^\ddagger/k_BT}$$

This relationship is useful for the qualitative interpretation of experimental A-factors. To see this, we note that the factor (ek_BT/h) has a value of $ca.$ $10^{13.5}$ s^{-1} (e.g., $A_\infty = 10^{13.53}$ s^{-1} at 600 K and $10^{13.75}$ s^{-1} at 1000 K) and therefore the value of an experimental A-factor may be related to the increase or decrease in entropy when going from the reactant molecule to the transition state. For instance, an A-factor of 10^{15} s^{-1} implies that $\Delta S^\ddagger$ is positive, i.e., the transition state has a greater entropy than the molecule. In this way "tight" transition states (such a four-centre transition state) are commonly associated with a decrease in entropy in going from reactant to transition state, whereas "loose" transition states (such as a simple-fission transition state) are associated with an increase in entropy. These relations enable one to estimate of the magnitude of the A-factor for a reaction involving a particular type (e.g., three-centre, four-centre, $etc.$) of transition state for which experimental data are not available, as well as checking on the correctness of interpretation of extant data.

The A-factor and activation energy predicted from the transition state model could be obtained from a plot of the calculated high-pressure-limiting rate coefficient versus inverse temperature. However, it is possible to obtain a more direct analytical relationship between the transition state parameters and the Arrhenius parameters by making use of the transition state expression of equation 2.4.8. The activation energy, as noted above, is $defined$ by:

$$E_\infty = -k_B \frac{\partial \ln k_{uni}^\infty}{\partial 1/T} \tag{2.5.2}$$

Substituting for k_{uni}^∞ with equation 2.4.8 gives:

$$E_\infty = k_BT - k_B \frac{\partial \ln(Q^\dagger/Q)}{\partial 1/T} + E_0 \tag{2.5.3}$$

where E_∞ and E_0 are molecular quantities (conversion to molar quantities is carried out by multiplying by Avogadro's constant). The partition functions $Q^\dagger$ and Q in equation 2.5.3 are evaluated with respect to the zero-point energies of the transition state and reactant respectively.

We next derive the corresponding expression for the A-factor. From equation 2.5.1, we have:

$$\ln A_\infty = \ln k_{uni}^\infty + \frac{E_\infty}{k_BT} \tag{2.5.4}$$

Substituting for k_{uni}^∞ with equation 2.4.8 and for E_∞ with equation 2.5.3 gives:

$$\ln A_\infty = \ln\left(\frac{ek_BT}{h}\right) + \ln\frac{Q^\dagger}{Q} - \frac{1}{T}\frac{\partial \ln(Q^\dagger/Q)}{\partial 1/T} \tag{2.5.5}$$

The Arrhenius parameters can be expressed in a way that is conceptually useful by introducing the notion of the $enthalpy$ and the $entropy$ differences between the transition state and the reactant. These quantities are expressed in terms of the partition function as (e.g., McQuarrie, 1976):

$$H = -k_B \frac{\partial \ln Q_{tot}}{\partial 1/T} + Nk_BT \tag{2.5.6}$$

$$S = k_B \ln Q_{tot} - \frac{k_B}{T}\frac{\partial \ln Q_{tot}}{\partial 1/T} \tag{2.5.7}$$

where N is the total number of molecules in the ensemble, and Q_{tot} is the total molecular partition function. Now, since the transformation from the reactant to the transtion state does not change the number of molecules in the ensemble, the term Nk_BT is the same for both the transition state and the reactant. The enthalpy $difference$ between the transtion state and the reactant therefore reduces to:

$$\Delta H^\ddagger = E_0 - k_B \frac{\partial \ln Q^\dagger/Q}{\partial 1/T} \tag{2.5.8}$$

where the electronic and translational partition functions for the reactant and transition state cancel out, and the difference between the electronic and zero-point vibrational energies of the reactant and transition state is implicit in E_0. The entropy difference reduces to:

$$\Delta S^\ddagger = k_B \ln(Q^\dagger/Q) - \frac{k_B}{T}\frac{\partial \ln Q^\dagger/Q}{\partial 1/T} \tag{2.5.9}$$

Equations 2.4.8, 2.5.6 and 2.5.2 together give:

$$E_\infty = \Delta H^\ddagger + k_BT \tag{2.5.10}$$

Equations 2.4.8, 2.5.7 and 2.5.9 give:

$$A_\infty = \frac{ek_BT}{h} e^{\Delta S^\ddagger/k_B} \tag{2.5.11}$$

(Exercise 2.8). Equations 2.5.10 and 2.5.11 associate the enthalpy change in going to the transition state with the activation energy, and the entropy change with the A-factor. Note however that the $activation$ $energy,$ $critical$ $energy$ and $enthalpy$ of $activation$ are not $exactly$ the $same,$ tending to differ from each other by a few kJ mol^{-1}. As noted at the start of this section, equation 2.5.11 is useful in the qualitative interpretation of experimental A-factors. The use of equations 2.5.10 and 2.5.11 is exemplified in Exercise 2.9.

Equations 2.5.10 and 2.5.11 show that any frequencies that are the same in reactant and in transition state will have no effect on k_{uni}^∞, since equations 2.5.10 and 2.5.11 involve differences (however, those frequencies that are the same in reactant and transition state still affect the falloff curves, as will be seen in Chapter 6, because of their effects on the densities of states).

We now collect the expressions necessary for calculating the high-pressure A-factor from the frequencies and rotational constants (or moments of inertia) of the reactant and activated complex. From equation 2.5.11, this requires the entropy difference between activated complex and reactant, which is computed as follows from the corresponding partition functions. First, consider the rotational contributions. We shall give here a quite general expression, which, as well as