Using $\Delta G^\circ / RT = -\ln K$, we obtain

$$\boxed{\frac{d\ln K}{dT} = \frac{\Delta H^\circ}{RT^2}.}$$ (14.33)

This is known as the *van't Hoff* equation and gives the variation of the equilibrium constant with temperature. If K is known at a temperature T_0, it is obtained at any other temperature by integration:

$$\ln\frac{K(T)}{K(T_0)} = \int_{T_0}^{T} \frac{\Delta H^\circ}{RT^2} dT.$$ (14.34)

The integration is simplified if the standard enthalpy is assumed constant:

$$\int_{T_0}^{T} \frac{\Delta H^\circ}{RT^2} dT \approx -\frac{\Delta H^\circ}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right),$$ (14.35)
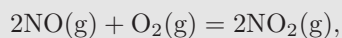
and the equilibrium constant at temperature T from eq. (14.34) becomes

$$\boxed{K(T) \approx K(T_0)\exp\left[-\frac{\Delta H^\circ}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right].}$$ (14.36)

Since small errors in ΔH° are amplified inside the exponential term, the proper procedure is to use eq. (14.8) to express ΔH° in terms of T, then integrate the resulting expression in terms of temperature.

Example 14.12: Equilibrium at Other Temperatures
Calculate the equilibrium constant of the reaction

$$2NO(g) + O_2(g) = 2NO_2(g),$$

at 1200 °C assuming the enthalpy of reaction to be constant.

Solution   The equilibrium constant for this reaction at 25 °C was calculated in Example 14.11 and was found to be

$$K_{298} = 2.23 \times 10^{12}.$$

The standard enthalpy of the reaction at 25 °C is calculated from the tabulated standard enthalpies of formation:

$$\Delta H^\circ_{298} = \underline{-114,140} \text{ J.}$$

-118140

-118140

Using eq. (14.36), the equilibrium constant at 1200 °C (1473.15 K) is

$$\ln \frac{K(T)}{K_{298}} = -\frac{(-114,140)}{8.314}\left(\frac{1}{1473.15} - \frac{1}{298.15}\right) = -36.7 \quad \Rightarrow$$

$$K(1473 \text{ K}) = K_{298} \times e^{-36.7} = 2.50 \times 10^{-4}.$$

Comments   Notice that the equilibrium constant decreases (and substantially so) with temperature. Indeed, from eq. (14.33) we expect that the equilibrium constant must decrease with temperature if the reaction is exothermic ($\Delta H < 0$).

Example 14.13: Heat of Reaction as a Function of Temperature
In the previous example, we assumed that $\Delta H°$ is constant in the range 25 °C to 1200 °C. Is this a good approximation?

Solution   To answer this question we will calculate the equilibrium constant by taking into account the variation of the standard heat of reaction. First, we will do this by an approximation, then by the most accurate calculation.

Approximate calculation. As an approximation, we will calculate the standard heat of reaction at 1200 °C and we will apply eq. (14.36) using an average value of $\Delta H°$ between 25 °C and 1200 °C. We collect the heat capacities of the reactants, which are given by the polynomial form,

$$\frac{C_P^{\text{ig}}}{R} = c_0 + c_1 T + c_2 T^2 + c_3 T^3 + c_4 T^4,$$

with T in kelvin given below:

	c_0	c_1	c_2	c_3	c_4
NO	4.534	−0.007644	0.00002066	-2.156×10^{-8}	8.06×10^{-12}
O_2	3.63	−0.001794	6.58×10^{-6}	-6.01×10^{-9}	1.79×10^{-12}
NO_2	3.2973	0.0033374	3.234×10^{-6}	-5.6799×10^{-9}	2.0855×10^{-12}

The term $\Delta C_P°$ is calculated from the above expressions. Since all heat capacities are given by the same polynomial form, $\Delta C_P°$ is also given as a fourth-order polynomial in T with coefficients c_i' given by

$$c_i' = \sum_j \nu_j c_i^{(j)}$$

where $c_i^{(j)}$ is the corresponding coefficient of species j and ν_j is its stoichiometric coefficient. Applying this equation to the values in the above table we find

$$\Delta C_P° = -50.7437 + 0.197514\,T - 0.000344466\,T^2 + 3.14021 \times 10^{-7}\,T^3 - 1.14226 \times 10^{-10}\,T^4.$$