APPENDIX 1

Calculation of reduction activation energy, E_r;

$$H_2 + O\,(S) \longrightarrow H_2O + \square$$

$$\text{Rate} = k\,[H_2]_m\,[O_s]$$

$$-d[H_2]_m = A\,\exp\left(\frac{-E_r}{RT}\right)[H_2]_m\,[O_s] \quad \text{........ (i)}$$

Solution of equation (i) at T_m gives;

$$\frac{-\,E_r}{RT_m^{\,2}} = \left(\frac{A}{\beta}\right)[H_2]_m\,\exp\left(\frac{-E_r}{RT}\right) \quad \text{........ (ii)}$$

From the Redhead equation;

$$k_1 = A\,\exp\left(\frac{-E_r}{RT}\right) \quad \text{........ (iii)}$$

Therefore from equation (ii),

$$k_2 = A[H_2]_m\,\exp\left(\frac{-E_r}{RT}\right) \quad \text{........ (iv)}$$

Since k_1 and k_2 are the same at T_m and let $k = \chi$ at T_m

$$\left(\frac{-E_r}{RT}\right) \qquad \left(\frac{-E_r}{RT}\right)$$

$$\frac{\chi}{A[H_2]_m} = \exp \qquad \text{or} \qquad \frac{A[H_2]_m}{\chi} = \exp$$

$$\frac{-E_r}{RT} = \ln\left(\frac{A[H_2]_m}{\chi}\right)$$

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$$\frac{-E_r}{RT} = RT_m \ln\left(\frac{A[H_2]_m}{\chi}\right)$$

For the peak maximum at 700 K;

$$E\alpha = T_m \times 0.066$$

$$= 700 \times 0.066$$

$$= 46.2 \text{ kcal mol}^{-1}$$

$$\chi = A \exp\left(\frac{-E_r}{RT}\right)$$

$$= 10^{13}\, s^{-1} \exp\left(\frac{-(46.2 \text{ kcal mol}^{-1})}{0.001987 \text{ kcal mol}^{-1} (700 \text{ K})}\right)$$

$$= 0.03754\, s^{-1}$$

$$[H_2]_m = \frac{n}{V} = \frac{0.05}{RT}$$

$$= \frac{0.05}{(82.056)(298)}$$

$$= 2.04 \times 10^{-6} \text{ mol cm}^{-3}$$

$$\frac{-E_r}{RT} = RT_m \ \text{In} \left(\frac{A[H_2]_m}{\chi} \right)$$

$$= 0.001987 \ \text{kcal K}^{-1} \ \text{mol}^{-1} \ (700 \ \text{K})$$

$$\text{In} \left(\frac{10^{13} \ \text{cm}^3 \ \text{mol}^{-1} \ \text{s}^{-1} \ (2.04 \times 10^{-6})}{0.03754 \ \text{s}^{-1}} \right)$$

$$= 31.2 \ \text{kcal mol}^{-1} \ (4.184 \ \text{J})$$

$$= 130.5 \ \text{kJ mol}^{-1}$$

$$(\text{kJ mol}^{-1} = 4.184 \ \text{kcal mol}^{-1})$$