Page 211, Remark 22

The proof of equation (e):

Equation (b) in Rem. 22 contains function:

$$\tilde{\Pi}_0 = \sum_{p=1}^{n-h} \lambda A^p \tilde{J}_p(T^o + \lambda\beta, B^{\sigma o} + \lambda\epsilon^\sigma, \lambda A^r) \equiv \sum_{p=1}^{n-h} \lambda A^p \tilde{J}_p(\cdots) \tag{1}$$

Then (b) is

$$\frac{\mathrm{d}\tilde{\Pi}_0}{\mathrm{d}\lambda} = \sum_{p=1}^{n-h} \left[A^p \tilde{J}_p(\cdots) + \lambda A^p \frac{\mathrm{d}\tilde{J}_p(\cdots)}{\mathrm{d}\lambda} \right] \tag{2}$$

and the second derivative in (c) is as follows:

$$\begin{aligned}
\frac{\mathrm{d}^2\tilde{\Pi}_0}{\mathrm{d}\lambda^2} &= \sum_{p=1}^{n-h} \left\{ \frac{\mathrm{d}}{\mathrm{d}\lambda} \left[A^p \tilde{J}_p(\cdots) \right] + \frac{\mathrm{d}}{\mathrm{d}\lambda} \left[\lambda A^p \frac{\mathrm{d}\tilde{J}_p(\cdots)}{\mathrm{d}\lambda} \right] \right\} \\
&= \sum_{p=1}^{n-h} A^p \left\{ \frac{\mathrm{d}}{\mathrm{d}\lambda} \tilde{J}_p(\cdots) + \frac{\mathrm{d}}{\mathrm{d}\lambda} \left[\lambda \frac{\mathrm{d}\tilde{J}_p(\cdots)}{\mathrm{d}\lambda} \right] \right\} \\
&= \sum_{p=1}^{n-h} A^p \left[\frac{\mathrm{d}}{\mathrm{d}\lambda} \tilde{J}_p(\cdots) + \frac{\mathrm{d}}{\mathrm{d}\lambda} \tilde{J}_p(\cdots) + \lambda \frac{\mathrm{d}^2}{\mathrm{d}\lambda^2} \tilde{J}_p(\cdots) \right] \\
&= \sum_{p=1}^{n-h} A^p \left[2 \frac{\mathrm{d}}{\mathrm{d}\lambda} \tilde{J}_p(\cdots) + \lambda \frac{\mathrm{d}^2}{\mathrm{d}\lambda^2} \tilde{J}_p(\cdots) \right] \\
&= \sum_{p=1}^{n-h} 2A^p \left[\left(\frac{\partial \tilde{J}_p}{\partial T} \right)^o \beta + \left(\frac{\partial \tilde{J}_p}{\partial B^\sigma} \right)^o \epsilon^\sigma + \sum_{r=1}^{n-h} \left(\frac{\partial \tilde{J}_p}{\partial A^r} \right)^o A^r + \frac{\lambda}{2} \frac{\mathrm{d}^2}{\mathrm{d}\lambda^2} \tilde{J}_p(\cdots) \right]
\end{aligned} \tag{3}$$

Equation (c) in Rem. 22 should be valid for arbitrary values of β, ϵ^σ, i.e., also for $\beta = \epsilon^\sigma = 0$. Substitution these values (together with $\lambda = 0$) into the last equation in (3) yields inequality (e) in Rem. 22.

The inequality (e) is another restriction put by thermodynamics on reaction kinetics and is not seen in other works. However, it seems that explicit consequences, e.g. for rate constants, can be derived only for very simple reactions.[1]

[1] PEKAŘ, M. Thermodynamic analysis of chemically reacting mixtures and their kinetics – example of a mixture of three isomers. *ChemPhysChem*, 2016, vol. 17, no. 20, p. 3333-3341.