Determination of the reaction entropy of elementary modes

The reaction entropy of individual elementary modes ΔS_i (kJ/K-mole) is computed based on the stoichiometric equation of elementary modes. The reaction entropy is given by

$$\Delta S_i = \sum_{m=1}^{k} v_{i,m} S_{i,m} \tag{1}$$

where v_m is the stoichiometry coefficient of species m in the overall reaction of elementary mode i containing k reactants, and S_m (kJ/K-mole) is the entropy of formation of species m.

The entropy of formation can be computed using the Gibbs equation

$$S_m = \frac{H_m - G_m}{T} \tag{2}$$

where T is the absolute temperature at the condition considered, H_m (kJ/mole) is the molar enthalpy of formation for the species m, and G_m (kJ/mole) is the molar Gibbs free energy of formation of the species m.

The enthalpy and free energy of formation for each species m can be computed from

$$H_m = H_m^{\text{o}} + \int_{298}^{T} C_{P,m} dT \tag{3}$$

$$G_m = G_m^{\text{o}}(T) + RT \ln c_m \tag{4}$$

where $C_{P,m}$ (kJ/K-mole) is the heat capacity of species m at constant pressure. H_m^{o} is the standard enthalpy of formation at 298 K. $G_m^{\text{o}}(T)$ is the standard free energy of formation

for 1 mole. R (kJ/K-mole) is the universal gas constant, and c_m is the molar concentration

of species m.

The Gibbs free energy $G_m^o(T)$ is related to the equilibrium constant by

$$G_m^o(T) = -RT \ln K \tag{5}$$

where K is the equilibrium constant.

The temperature dependence of the equilibrium constant is described by the van't Hoff

equation

$$\frac{d \ln K}{dT} = \frac{\Delta H^o}{RT^2} \tag{6}$$

Because the heat of reaction does not vary much with temperature over a small

temperature range it can be approximated to be constant and Eq (5) can be integrated to

result in

$$G_m^o(T) = T \left(\frac{\Delta G^o - \Delta H^o}{298} + \frac{\Delta H^o}{T} \right) \tag{7}$$

Substituting Eq (3) and (4) into (2) gives the entropy of formation of species m

$$S_m = \frac{1}{T} \left(H_m^o + \int_{298}^{T} C_{P,m} dT - G_m^o(T) - RT \ln c_m \right) \tag{8}$$

The reaction entropy of individual elementary modes thus becomes

$$\Delta S_i = \frac{1}{T} \sum_{m=1}^{k} \nu_{i,m} \left(H_{i,m}^o + \int_{298}^{T} C_{P\,i,m} dT - G_{i,m}^o(T) - RT \ln c_{i,m} \right) \tag{9}$$

The reaction entropy can be estimated from the standard molar values of the enthalpy and

free energy since the terms involving the heat capacity and the species concentration are

very small compared to the other terms for the compounds considered in this study. The

standard values of enthalpy and free energy can be estimated using the degree of

reduction correlations given in Sandler and Orbey (1991). The rate of entropy production

of individual elementary modes is given by

$$r_{\Delta S_i} = \Delta S_i \cdot r_g \tag{10}$$

where r_g is the rate of glucose uptake (mole/l-hr).