EQUILIBRIA IN ELECTROCHEMISTRY AND MAXIMAL RATES OF REACTION

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Abstract. We consider Gibbs' definition of chemical equilibrium and connect it with dynamic equilibrium, in terms of no substance formed. We determine the activity coefficient as a function of temperature and pressure, in reactions with or without interaction of a solvent, incorporating the error terms from Raoult's Law and Henry's Law, if necessary. We compute the maximal reaction paths and apply the results to electrochemistry, using the Nernst equation.

1. Introduction

This paper is divided into 14 sections. In section 2, we give some basic definitions, and derive the Nernst equation for the standard cell. We prove some results about the activity coefficient Q, assuming an idealised law in the behaviour of the activities and chemical potentials, $\mu_i = \mu_i^\circ + RTln(a_i)$, for $1 \leq i \leq c$, with c substances, which holds throughout the section. In Lemma 2.11, we use the van't Hoff, Gibbs-Helmholtz equations to find an expression for $\Delta G^\circ(T)$ along quasi-chemical equilibrium paths. In Lemma 2.12, we use an entropy calculation to find $(\frac{\partial G}{\partial \xi})_{T,P}$ and combine the result with Lemma 2.11 to calculate the activity coefficient Q. In Lemma 2.17, we prove every straight line chemical equilibrium path is a dynamic equilibrium path, partially confirming a speculation of Gibbs. The method of constant Q along a path implying dynamic equilibrium is repeatedly used and generalised later in the paper. The question of the existence of feasible paths for a reaction, given a curve in the temperature/pressure plane, is answered in Lemma 2.19 and again later generalised.

In Section 3, we consider ideal solutions and introduce a fixed error term from Raoult's law. The results from section 0 generalise and in Lemma 3.6, we find the paths of maximal reaction, in the sense of maximising extent ξ, implicitly, in terms of temperature and pressure (T, P). We apply the results to electrochemistry in Section 4. In Section 5, we consider dilute solutions, adding substance 0, and consider the definition of Q, involving the activity a_0, obtaining the formula

for the activity coefficient in Lemma 5.2. In Section 6, we consider dilute solutions with interaction of the solvent, in which the solvent is ideal and the solutes obey Henry's law, introducing a new fixed error term in Definition 6.1, and obtaining the maximal reaction paths in Lemma 6.7. In Section 7, we check that the calculation of $(\frac{\partial G}{\partial \xi})_{T,P}$ is not effected when introducing fugacity. In Section 8, we introduce new fixed error terms from fugacity, in Definition 8.1. We alter the conventional definition of Q to incorporate fugacity in the error term and obtain the paths of maximal reaction in Lemma 8.7. We apply the results to electrochemistry in Section 9, in particular the reaction in catalyzers, and give a strategy for improving the efficiency of hydrogen and oxygen production from water in Remarks 12.5. In Section 10, we consider the case when there is no interaction of the solvent, and in Sections 10 and 11, we derive the main results quickly by altering Q to ignore the activity a_0. However, it an interesting but difficult exercise to try and derive the results using the definition in Section 5. We suggest the results here could be used in maximising ethanol production. We gain apply the results to electrochemistry in Section 12, in particularly the standard cell. In Section 13, we reconsider the assumption that $\Delta H^\circ(T)$ is constant, made throughout the paper. We show that by increasing the mass of the mixture, in particularly the amount of solvent, we can make the error involved here disappear in the limit. Finally, in Section 14, we consider independence and existence of paths.

2. The Idealised Case

Definition 2.1. *For c substances, we define the Gibbs energy $G(T, P, n_1, \dots, n_c)$ by;*

$$G = U + PV - TS$$

where U is the internal energy, P is pressure, V is volume, T is temperature and S is entropy. We define the enthalpy $H(T, P, n_1, \dots, n_c)$ by;

$$H = U + PV = G + TS$$

see [9] *and* [5]*. We define the Gibbs energy at standard pressure $G^\circ(T, n_1, \dots, n_c) = G(T, P^\circ, n_1, \dots, n_c)$, where P° is the standard pressure. We define the chemical potentials, $1 \leq i \leq c$, by;*

$\mu_i(T,P) = (\frac{\partial G}{\partial n_i})_{T,P,n'}$

where n_i *is the amount of substance* i *measured in moles, and* T, P, n' *fixes the pressure, temperature and the amount of every substance except substance* i.

We consider an electrolyte as a solute in a dilute solution and define the activities a_i, $1 \leq i \leq c$, *by;*

$a_1 = \gamma_1 x_1 \simeq 1$

$a_i = \frac{\gamma_i m_i}{m^\circ}$ $(2 \leq i \leq c)$

where the molality $m_i = \frac{n_i}{w_1}$, *and* w_1 *is the mass of the solvent, component* 1, $m^\circ = 1$, $x_i = \frac{n_i}{n}$, $n = \sum_{i=1}^{c} n_i$, $\gamma_i, 1 \leq i \leq c$, *are the activity coefficients,* $c_i = \frac{n_i}{V}$, $c^\circ = 1$, *and the activity quotient;*

$Q = \prod_{i=1}^{c} a_i^{\nu_i}$

where ν_i, *for* $1 \leq i \leq c$ *are the stoichiometric coefficients.*

We have, for a solute in a dilute solution, that $\mu_i = \mu_i^\circ + RTln(a_i)$, *see* [9], *noting that* μ_i *is independent of the amount of substance* n_i, *and* μ_i° *in the molality description is equal to* $\mu_i^{(m)}$, *where* m_i *is equal to* $m^\circ = 1$ *in a hypothetical solution.*

We define $\Delta G^\circ(T)$ *and* $\Delta H^\circ(T)$ *to be the changes in Gibbs energy and enthalpy at standard pressure* P° *and temperature* T, *for* 1 *mole of reaction, see* [1]*and* [4].

We define the extent $\xi(T,P)$ *of a reaction by;*

$n_{i,0} + \nu_i \xi = n_i$

where $n_{i,0} = n_i(initial)$. *We assume that if;*

$h_{T,P,n_{1,0},\ldots,n_{c,0}}(\xi) = G(T, P, n_{1,0} + \nu_1\xi, \ldots, n_{c,0} + \nu_c\xi)$

then $\frac{dh_{T,P,n_{1,0},\ldots,n_{c,0}}}{d\xi}(\xi)$ *is independent of* $\{n_{1,0}, \ldots, n_{c,0},\} \subset \mathcal{R}_{>0}$ *and* $\xi \in \mathcal{R}_{\geq 0}$, *and define this as* $(\frac{\partial G}{\partial \xi})|_{T,P}$.

We define chemical equilibrium by $(\frac{\partial G}{\partial \xi})|_{T,P} = 0$, *and dynamic equilibrium by a path* $\gamma : [0,1] \to (T, P, n_1, \ldots, n_c)$, *such that* $n_i'(t) =$

$pr_{2+i}(\gamma)'(t) = 0$, *for* $1 \leq i \leq c$, *so that no substance is formed.*

We define $E(T, P, n_1, \ldots, n_c)$ *to be the potential in the standard cell and* $E^\circ(T, n_1, \ldots, n_c) = E(T, P^\circ, n_1, \ldots, n_c)$ *to be the potential at* P°. *We let* F *denote Faraday's constant,* $R = N_A k$ *the gas constant, where* N_{Av} *is Avogadro's constant and* k *is Boltzmann's constant. We have that* $N = N_{Av} n$, *where* N *is the number of particles,* n *is the amount in moles. We define the electric potential* ϕ *by* $\overline{E} = - \bigtriangledown (\phi)$, e *is the charge on an electron,* z_i *is the valence of an ion.*

Remarks 2.2. *The idea that* $(\frac{\partial G}{\partial \xi})|_{T,P}$ *can depend on the composition or molar amounts for dilute solutions seems a bit strange. If so, we could find a pair* $\{(n_1, \ldots, n_c), (n_1', \ldots, n_c')\}$ *such that;*

$$(\tfrac{\partial G}{\partial \xi})|_{T,P}(n_1, \ldots, n_c) > (\tfrac{\partial G}{\partial \xi})|_{T,P}(n_1', \ldots, n_c')$$

If the reaction is reversible, we can encourage the reverse reaction of 1 *mole at* $(T, P, n_1', \ldots, n_c')$, *to obtain* $\Delta G = -(\frac{\partial G}{\partial \xi})|_{T,P}(n_1', \ldots, n_c')$, *and then change the composition and encourage the forward reaction of* 1 *mole at* $(T, P, n_1, \ldots, n_c)$, *with* $\Delta G' = (\frac{\partial G}{\partial \xi})|_{T,P}(n_1, \ldots, n_c)$. *The total Gibbs free energy change* $\Delta G'' = \Delta G + \Delta G'$ *at* (T, P) *is then* $(\frac{\partial G}{\partial \xi})|_{T,P}(n_1, \ldots, n_c) - (\frac{\partial G}{\partial \xi})|_{T,P}(n_1', \ldots, n_c') > 0$ *with no substance formed, so that we have gained energy with no reaction. Forward and reverse reactions can be obtained easily in electrolysis of water, with the electrolysis reaction being encouraged by applying a potential to the anode and cathode, and the reverse fuel cell reaction being encouraged by attaching a load to the cell. The increase in Gibbs free energy means we could drive a motor as the load without power, contradicting the first law of thermodynamics, unless we require that power is used to change the amount of solvent, water, and the amounts of dissolved oxygen and hydrogen. Thermal energy can be converted perfectly to evaporate and condense water, as well as the solutions, with very little volume change, the change in solvent and solution amount then driving the motor. This would contradict the second law of thermodynamics, that to find "A transformation whose only final result is to transform into work heat extracted from a source which is at the same temperature throughout is impossible", see* [5] *and accompanying footnote on p30. We can make this idea more precise in the following lemma.*

Lemma 2.3. *For a dilute solution,* $\frac{\partial G}{\partial \xi}$ *only depends on temperature and pressure, if we assume the number of moles of each component is*

very large.

Proof. By a result in [5], for a dilute solution, with substance 0 as the solvent, substances $1 \leq i \leq g$ as the solutes, the entropy is calculated as;

$S(T, P, n_0, \ldots, n_g) \simeq \sum_{i=0}^{g} n_i s_i(T, P) - R \sum_{i=0}^{g} n_i log(x_i)$

where $x_i = \frac{n_i}{n}$, and;

$s_i(T, P) = C_{P_i} log(T) - Rlog(P) + a_i + Rlog(R)$, $0 \leq i \leq g$

It follows from the calculation of internal energy U and volume V for dilute solutions, that the Gibbs free energy is given by;

$G(T, P, n_0, \ldots, n_g) = U + PV - TS$

$= \sum_{i=0}^{g} n_i(f_i(T, P) + Pv_i(T, P)) + RT \sum_{i=0}^{g} n_i log(x_i)$

where $f_i(T, P) = u_i(T, P) - Ts_i(T, P)$,

$U = \sum_{i=0}^{g} n_i u_i(T, P)$, $V = \sum_{i=0}^{g} n_i v_i(T, P)$

so we have that;

$\frac{\partial G}{\partial \xi} = \sum_{i=0}^{g} \nu_i \mu_i$

$= \sum_{i=0}^{g} \nu_i \frac{\partial G}{\partial n_i}$

$= \sum_{i=0}^{g} \nu_i(f_i(T, P) + Pv_i(T, P)) + RT \sum_{i=0}^{g} \nu_i \frac{\partial}{\partial n_i} [\sum_{i=0}^{g} n_i log(x_i)]$

We have that;

$\frac{\partial}{\partial n_i} [\sum_{i=0}^{g} n_i log(x_i)]$

$= log(x_i) + \frac{n_i}{x_i}(\frac{1}{n} - \frac{n_i}{n^2}) + \sum_{j \neq i} \frac{n_j}{x_j}(-\frac{n_j}{n^2})$

$= log(x_i) + n(\frac{1}{n} - \frac{n_i}{n^2}) + \sum_{j \neq i} n(-\frac{n_j}{n^2})$

$= log(x_i) + 1 - x_i - \sum_{j \neq i} x_j$

$= log(x_i) + 1 - \sum_{i=0}^{g} x_i$

$= log(x_i)$

so that;

$\frac{\partial G}{\partial \xi} = \sum_{i=0}^{g} \nu_i (f_i(T,P) + Pv_i(T,P)) + RT \sum_{i=0}^{g} \nu_i log(x_i)$

Then;

$\frac{\partial^2 G}{\partial \xi \partial n_i} = RT \frac{\partial}{\partial n_i} (\sum_{i=0}^{g} \nu_i log(x_i))$

$= RT(\sum_{j \neq i} \frac{\nu_j}{x_j}(-\frac{n_j}{n^2}) + \frac{\nu_i}{x_i}(\frac{1}{n} - \frac{n_i}{n^2}))$

$= RT(\sum_{j \neq i} -\frac{\nu_j}{n} + \frac{\nu_i}{n_i} - \frac{\nu_i}{n})$

$= -\frac{RT}{n}(\sum_{i=0}^{g} \nu_i) + \frac{RT\nu_i}{n_i}$

$\simeq 0, \ (0 \leq i \leq g)$

if $n_0, \ldots n_g >> 0$

and we can conclude that $\frac{\partial G}{\partial \xi}$ approximately only depends on temperature and pressure (T, P).

□

Remarks 2.4. *Principle of mass action*

It follows that we can treat $\sum_{i=0}^{g} \nu_i log(x_i)$ *as a constant in the formula for* $\frac{\partial G}{\partial \xi}$ *and suppose that the chemical potentials are functions of temperature and pressure only. Using the formula for the activities of a dilute solution;*

$\mu_i(T,P) = \mu_i(T,P^\circ) + RTln(x_i)(T,P)$

which is derived differently from Fermi's calculation of entropy, we argue below and in the paper [13]*, that we can make this formula consistent by including error terms* $x_i(T,P^\circ)$*. Then we have that;*

$\frac{\partial G}{\partial \xi}(T,P) - \frac{\partial G}{\partial \xi}(T,P^\circ) = RTln(\frac{Q(T,P)}{Q_0(T,P^\circ)})$

where the constant term $RT\sum_{i=0}^{g}\nu_i log(x_i)$ *cancels out in the difference* $\frac{\partial G}{\partial \xi}(T,P)-\frac{\partial G}{\partial \xi}(T,P^\circ)$. *We calculate the functions* $f_i(T,P)$ *below as only depending on* T *and obtain the formula;*

$\frac{Q(T,P)}{Q_0(T,P^\circ)}=e^{\frac{\epsilon(P-P^\circ)}{RT}}$, $(*)$

If $Q_0(T,P^\circ)$ *is determined by Fermi's law of mass action, then so is* $Q(T,P)$, *as we have that, at chemical equilibrium;*

$0=\frac{\partial G}{\partial \xi}(T,P,\overline{n}(T,P))=\sum_{i=0}^{g}\nu_i(f_i(T,P)+Pv_i(T,P))+RT\sum_{i=0}^{g}\nu_i log(x_i)$

$=F(T)+\epsilon P+RT\sum_{i=0}^{g}\nu_i log(x_i)$

so that, for the predictions of mass action;

$Q(T,P)=e^{\frac{-F(T)-\epsilon P}{RT}}$

$Q(T,P^\circ)=e^{\frac{-F(T)-\epsilon P^\circ}{RT}}$ $(**)$

and, by $(*)$, *with the formula in* $(**)$ *for* Q_0;

$Q(T,P)=Q(T,P^\circ)e^{\frac{\epsilon(P-P^\circ)}{RT}}$

$=e^{\frac{-F(T)-\epsilon P^\circ}{RT}}e^{\frac{\epsilon(P-P^\circ)}{RT}}$

$=e^{\frac{-F(T)+\epsilon(P-2P^\circ)}{RT}}$

$\simeq e^{\frac{-F(T)-\epsilon P}{RT}}$

at $P\simeq P^\circ$.

As ϵ *is negative for water electrolysis, see below, we found it necessary, see Remarks 3.11, to reverse the sign of* ϵ *at high voltages, and use the formula;*

$\frac{Q(T,P)}{Q_0(T,P^\circ)}=e^{\frac{-\epsilon(P-P^\circ)}{RT}}$, $(***)$

Then, repeating the calculation above with the same law of mass action $(**)$, *using* $(***)$ *instead;*

$$Q(T,P) = Q(T,P^\circ)e^{\frac{-\epsilon(P-P^\circ)}{RT}}$$

$$= e^{\frac{-F(T)-\epsilon P^\circ}{RT}} e^{\frac{-\epsilon(P-P^\circ)}{RT}}$$

$$= e^{\frac{-F(T)-\epsilon P}{RT}}$$

which is in agreement. In both cases, we do NOT *violate the principle of mass action.*

Lemma 2.5. $dG = -SdT + VdP + \sum_{i=1}^{c} \mu_i dn_i$

Proof. We have, by the definition of the chemical potential and the laws of differentials, that;

$$dG = \frac{\partial G}{\partial T}_{P,n} dT + \frac{\partial G}{\partial P}_{T,n} dP + \sum_{i=1}^{c} \frac{\partial G}{\partial n_i}_{T,P,n'} dn_i$$

$$= \frac{\partial G}{\partial T}_{P,n} dT + \frac{\partial G}{\partial P}_{T,n} dP + \sum_{i=1}^{c} \mu_i dn_i, \ (*)$$

Fixing n, using $G = U + PV - TS$, the first law of thermodynamics, $dU = dQ - PdV$, the definition of entropy, $dQ = TdS$, the product rule for differentials, and $(*)$, we have that;

$$dU = TdS - PdV$$

$$dG = dU + VdP + PdV - SdT - TdS$$

$$= (TdS - PdV) + VdP + PdV - SdT - TdS$$

$$= -SdT + VdP$$

$$dG = \frac{\partial G}{\partial T}_{P,n} dT + \frac{\partial G}{\partial P}_{T,n} dP \ (**)$$

so that, from $(**)$, and equating coefficients, $\frac{\partial G}{\partial T}_{P,n} = -S$, $\frac{\partial G}{\partial P}_{T,n} = V$. Substituting into $(*)$, we obtain that;

$$dG = -SdT + VdP + \sum_{i=1}^{c} \mu_i dn_i$$

□

Definition 2.6. *We define electrical chemical equilibrium by* $(\frac{\partial G}{\partial \xi})_{T,P} = 0$ *where* G *is the Gibbs energy function for a charged and uncharged species.*

Lemma 2.7. *The Nernst Equation for the Standard Cell*

At electrical chemical equilibrium (T, P) *and* (T, P°)*;*

$E - E^{\circ} = -\frac{RTln(Q)}{2F}$

See [9].

Proof. For c substances, with c' the number of the charged species,using Definition 2.1, we have that the electrostatic potential energy;

$U_{el} = \sum_{i=1}^{c'} \phi(\overline{x}_i)q_i$, where $q_i = N_i e z_i = N_A n_i e z_i$

where $\{\overline{x}_i : 1 \leq i \leq c'\}$ are the positions of the charged species, N_i is the number of particles at $\overline{x}_i$.

We have that;

$U = U_{chem} + U_{el}$, so that;

$G(T, P, n_1, \ldots, n_c) = U + PV - TS$

$= U_{chem} + U_{el} + PV - TS$

$= U_{el} + G_{chem}$

$= \sum_{j=1}^{c} \phi(\overline{x}_j)q_j + G_{chem}$

$= \sum_{j=1}^{c} \phi(\overline{x}_j)N_A n_j e z_j + G_{chem}$

so that;

$\mu_i = (\frac{\partial G}{\partial n_i})_{T,P}$

$= (\frac{\partial(\sum_{j=1}^{c} \phi(\overline{x}_j)N_A n_j e z_j + G_{chem})}{\partial n_i})_{T,P}$

$= \mu_{i,chem}$, $(c' + 1 \leq i \leq c)$

$= \mu_{i,chem} + \frac{\partial(\phi(\overline{x}_i)N_A n_i e z_i)}{\partial n_i}$, $(1 \leq i \leq c')$

$= \mu_{i,chem} + \phi(\overline{x}_i)N_A e z_i$

$= \mu_{i,chem} + \phi(\overline{x}_i)F z_i$, $(*)$

We consider the standard cell reaction $H_2(g)+2AgCl(s)+2e^-(R) \rightarrow 2HCl+2Ag(s)+2e^-(L)$. At chemical equilibrium, similarly to Lemma 2.10, generalised to a collection involving charged species, using $(*)$, we have that;

$(\frac{\partial G}{\partial \xi})_{T,P} = \sum_{i=1}^{c} \nu_i \mu_i$

$= 2\mu(HCl) + 2\mu(Ag) - \mu(H_2) - 2\mu(AgCl) + 2\mu(e^-(L)) - 2\mu(e^-(R))$

$= (\frac{\partial G_{chem'}}{\partial \xi})_{T,P} + 2\mu(e^-(L)) - 2\mu(e^-(R))$

$= (\frac{\partial G_{chem'}}{\partial \xi})_{T,P} + ((2\mu_{chem}(e^-(L)) - 2F\phi(L)) - (2\mu_{chem}(e^-(L)) - 2F\phi(R)))$

$= (\frac{\partial G_{chem'}}{\partial \xi})_{T,P} + 2F(\phi(R) - \phi(L))$

$= (\frac{\partial G_{chem'}}{\partial \xi})_{T,P} + 2EF = 0$ $(\dagger)$

where $G_{chem'}$ is the Gibbs energy restricted to the uncharged species. We have that;

$(\frac{\partial G_{chem'}}{\partial \xi})_{T,P^\circ} = \sum_{i=c'+1}^{c} \nu_i \mu_i^\circ$

$= (\Delta G^\circ_{chem'} + RTln(Q_{chem'}(T, P^\circ)))$

$= \Delta G^\circ_{chem'}$, $(\dagger\dagger)$

using the definition of $Q_{chem'}$ in Definition 2.1, the fact that $\mu_i = \mu_i^\circ + RTln(a_i)$, $\mu_i = \mu_i^\circ$, for $c' + 1 \leq i \leq c$, so that $Q_{chem'}(T, P^\circ) = 1$.

From $(\dagger), (\dagger\dagger)$, we obtain;

$2E^\circ F = -(\frac{\partial G_{chem'}}{\partial \xi})_{T,P^\circ}$

$= -\Delta G^{\circ}_{chem'}$ $(\dagger\dagger\dagger)$

Similarly, we have that;

$(\frac{\partial G_{chem'}}{\partial \xi})_{T,P} = \sum_{i=c'+1}^{c} \nu_i \mu_i$

$= (\Delta G^{\circ}_{chem'} + RTln(Q_{chem'}(T,P)))$, $(\dagger\dagger\dagger\dagger)$

so from $(\dagger), (\dagger\dagger\dagger\dagger))$, we obtain that;

$2EF = -(\frac{\partial G_{chem'}}{\partial \xi})_{T,P}$

$= -(\Delta G^{\circ}_{chem'} + RTln(Q_{chem'}(T,P)))$, $(\sharp)$

Combining $(\sharp), (\dagger\dagger\dagger)$, we obtain that;

$2EF - 2E^{\circ}F = -(\Delta G^{\circ}_{chem'} + RTln(Q_{chem'}(T,P))) - (-\Delta G^{\circ}_{chem'})$

$= -RTln(Q_{chem'}(T,P))$

so that;

$E - E^{\circ} = -\frac{RTln(Q_{chem'}(T,P))}{2F}$

□

Lemma 2.8. *For the energy function G involving only an uncharged species;*

$(\frac{\partial G}{\partial \xi})_{T,P} = \Delta G^{\circ} + RTln(Q)$

see [9].

Proof. By Lemma 2.10, we have that;

$(\frac{\partial G}{\partial \xi})_{T,P} = \sum_{i=1}^{c} \nu_i \mu_i$

$\Delta G^{\circ} = \sum_{i=1}^{c} \nu_i \mu_i^{\circ}$, $(*)$

Using $(*)$, the fact that $\mu_i = \mu_i^{\circ} + RTln(a_i)$, and Definition 2.1, we have that;

$(\frac{\partial G}{\partial \xi})_{T,P} - \Delta G^\circ = \sum_{i=1}^{c} \nu_i(\mu_i - \mu_i^\circ)$

$= \sum_{i=1}^{c} \nu_i(\mu_i^\circ + RTln(a_i) - \mu_i^\circ)$

$= \sum_{i=1}^{c} \nu_i RTln(a_i)$

$= RTln(\prod_{i=1}^{c} a_i^{\nu_i}) = RTln(Q)$

□

Lemma 2.9. *At electrical chemical equilibrium (T, P) and (T, P°), and chemical equilibrium (T, P);*

$\Delta G^\circ = 2F(E - E^0)$

Proof. By Lemma 2.7, we have that;

$E - E^\circ = -\frac{RTln(Q)}{2F}$, $(*)$

and, by Lemma 2.8, we have that;

$0 = (\frac{\partial G}{\partial \xi})_{T,P} = \Delta G^\circ + RTln(Q)$, $(**)$

Rearranging $(*), (**)$, we obtain the result.

□

Lemma 2.10. *We have that;*

$(\frac{\partial G}{\partial \xi})_{T,P} = \sum_{i=1}^{c} \nu_i \mu_i$

$\Delta G^\circ = \sum_{i=1}^{c} \nu_i \mu_i^\circ$

At chemical equilibrium T, P, $(\frac{\partial G}{\partial \xi})_{T,P} = 0$ and at T, P^0, $\Delta G^\circ = 0$.

If chemical and electrical chemical equilibrium exists at (T, P°) and (T, P), $Q(T, P) = 1$. and $E = E^\circ$. Conversely, if $Q(T, P) = 1$ and chemical equilibrium exists at (T, P°) then chemical equilibrium exists at (T, P).

Chemical equilibrium exists at (T, P) iff $Q(T, P) = e^{\frac{-\Delta G^\circ}{RT}}$

We always have that $Q(T, P^\circ) = 1$.

Proof. For the first claim, we have, using the definition of ξ, that;

$dn_i = \nu_i d\xi$, $(1 \leq i \leq c)$, $(*)$

By Lemma 2.5, fixing T and P, and using $(*)$, we have that;

$dG = \sum_{i=1}^{c} \mu_i dn_i$

$= (\sum_{i=1}^{c} \mu_i \nu_i) d\xi$, $(\dagger)$

so that;

$(\frac{\partial G}{\partial \xi})_{T,P} = \sum_{i=1}^{c} \mu_i \nu_i$, $(\dagger\dagger)$

The second claim from the first, as;

$\Delta G^\circ(T) = \int_0^1 (\frac{\partial G}{\partial \xi})_{T,P^\circ}$

$= \int_0^1 (\sum_{i=1}^{c} \nu_i \mu_i^\circ(T)) d\xi$

$= \sum_{i=1}^{c} \nu_i \mu_i^\circ(T) \int_0^1 d\xi$

$= \sum_{i=1}^{c} \nu_i \mu_i^\circ(T)$

noting that $(\frac{\partial G}{\partial \xi})_{T,P^\circ}$ doesn't vary with ξ. For the third claim, at chemical equilibrium, T, P, noting again that $(\frac{\partial G}{\partial \xi})_{T,P}$ doesn't vary with ξ, and using $(\dagger, \dagger\dagger)$, we have that;

$dG = (\frac{\partial G}{\partial \xi})_{T,P} = 0$, (independently of ξ) $(\dagger\dagger\dagger)$

At chemical equilibrium T, P°, using the first and second claims, and $(\dagger\dagger\dagger)$, we have that;

$dG = (\frac{\partial G}{\partial \xi})_{T,P^\circ}$

$= \sum_{i=1}^{c} \nu_i \mu_i^\circ$

$= \Delta G^\circ = 0$

For the second to last claim, and the first direction, we have, by Lemma 2.8, that $RTln(Q) = 0$, so that $Q = 1$, and, by Lemma 2.7, that $E - E^\circ = -\frac{RTln(Q)}{2F} = 0$. For the converse, we have by Lemma 2.8, using the fact that $Q(T, P) = 1$;

$(\frac{\partial G}{\partial \xi})_{T,P} = \Delta G^\circ$

and, if chemical equilibrium exists at (T, P°), then, as $Q(T, P^\circ) = 1$ we have that;

$(\frac{\partial G}{\partial \xi})_{T,P^\circ} = \Delta G^\circ + RTln(Q) = \Delta G^\circ = 0$

so that $(\frac{\partial G}{\partial \xi})_{T,P} = 0$

For the penultimate claim, in one direction, use Lemma 2.8, together with the fact that $(\frac{\partial G}{\partial \xi})_{T,P} = 0$ and rearrange, the converse is also clear, applying ln.

For the final claim, we have, by the definition of activities, that;

$\mu_i = \mu_i^\circ + RTln(a_i)$

so that $a_i(T, P^\circ) = 1$. Now use the definition of Q in Definition 2.1.

□

Lemma 2.11. *van't Hoff,Gibbs-Helmholtz*

Along a chemical equilibrium path, we have that;

$ln(\frac{Q(T_2)}{Q(T_1)}) = \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^\circ}{T^2} dT$

$\frac{\Delta G^\circ(T_2)}{T_2} - \frac{\Delta G^\circ(T_1)}{T_1} = -\int_{T_1}^{T_2} \frac{\Delta H^\circ}{T^2} dT$

In particularly, if ΔH° is temperature independent;

$ln(\frac{Q(T_2)}{Q(T_1)}) = -\frac{\Delta H^\circ}{R}(\frac{1}{T_2} - \frac{1}{T_1})$

$\frac{\Delta G^\circ(T_2)}{T_2} - \frac{\Delta G^\circ(T_1)}{T_1} = \Delta H^\circ(\frac{1}{T_2} - \frac{1}{T_1})$

$\Delta G^\circ(T_1) = \frac{T_1}{T_2}\Delta G^\circ(T_2) - (\frac{T_1}{T_2} - 1)\Delta H^\circ$

For $c \in \mathcal{R}$, Let D_c intersect the line $P = P^\circ$ at (T_1, P°), then, for $(T_2, P) \in D_c$, we have that;

$Q(T_2, P) = e^{\frac{\Delta G^\circ(T_1) - \Delta G^\circ(T_2)}{RT_2}}$ (†††)

$c = \Delta G^\circ(T_1)$

$ln(\frac{Q(T_2)}{Q(T_1)}) = ln(Q(T_2)) = \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^\circ - c}{T^2} dT$

$\frac{\Delta G^\circ(T_2) - \Delta G^\circ(T_1)}{T_2} = -\int_{T_1}^{T_2} \frac{\Delta H^\circ - c}{T^2} dT$

and if ΔH° is temperature independent;

$ln(\frac{Q(T_2)}{Q(T_1)}) = ln(Q(T_2)) = -(\frac{\Delta H^\circ - c}{R})(\frac{1}{T_2} - \frac{1}{T_1})$ (††)

$\frac{\Delta G^\circ(T_2) - \Delta G^\circ(T_1)}{T_2} = (\Delta H^\circ - c)(\frac{1}{T_2} - \frac{1}{T_1})$ (†)

$\Delta G^\circ(T_1) = \frac{T_1}{T_2}\Delta G^\circ(T_2) - \Delta H^\circ(\frac{T_1}{T_2} - 1)$ (††††)

See also [9].

Proof. By Lemma 2.10, we have that;

$\Delta G^\circ = \sum_{i=1}^{c} \nu_i \mu_i^\circ$

so that differentiating with respect to T;

$\frac{d(\Delta G^\circ)}{dT} = \sum_{i=1}^{c} \nu_i \frac{d\mu_i^\circ}{dT}$

$= \sum_{i=1}^{c} \nu_i (\frac{\partial \mu_i^\circ}{\partial T})_{P,n}$

By Euler reciprocity, we have that;

$(\frac{\partial \mu_i^\circ}{\partial T})_{P,n} = -(\frac{\partial S^\circ}{\partial n_i})_{T,P,n'} = -\overline{S}_i^\circ$

so that, noting $\overline{S}_i^\circ$ is independent of n_i, so we can replace $\overline{S}_i^\circ$ by $\overline{S}_{m,i}^\circ$, the absolute molar entropy of substance i, and using thermodynamic arguments;

$\frac{d(\Delta G^\circ)}{dT} = -\sum_{i=1}^{c} \nu_i \overline{S}_i^\circ =$

$= -\sum_{i=1}^{c} \nu_i \overline{S}^{\circ}_{m,i}$

$= -\Delta S^{\circ}$ $(*)$

Using the product rule, $(*)$ and the definition of enthalpy, we have that;

$\frac{d}{dT}(\frac{\Delta G^{\circ}}{T}) = \frac{1}{T}\frac{d(\Delta G^{\circ})}{dT} - \frac{1}{T^2}\Delta G^{\circ}$

$= -\frac{\Delta S^{\circ}}{T} - \frac{\Delta G^{\circ}}{T^2}$

$= -\frac{\Delta (ST+G)^{\circ}}{T^2}$

$= -\frac{\Delta H^{\circ}}{T^2}$ $(**)$

By Lemma 2.10, along a chemical equilibrium path, we have that $Q = e^{\frac{-\Delta G^{\circ}}{RT}}$, so that $ln(Q) = \frac{-\Delta G^{\circ}}{RT}$. It follows from $(**)$ that;

$\frac{dln(Q)}{dT} = \frac{d}{dT}(\frac{-\Delta G^{\circ}}{RT})$

$= \frac{\Delta H^{\circ}}{RT^2}$

It follows, integrating between T_1 and T_2, that;

$ln(\frac{Q(T_2)}{Q(T_1)}) = ln(Q)(T_2) - ln(Q)(T_1)$

$= \frac{-\Delta G^{\circ}(T_2)}{RT_2} + \frac{\Delta G^{\circ}(T_1)}{RT_1}$

$= \int_{T_1}^{T_2} \frac{dln(Q)}{dT} dT$

$= \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^{\circ}}{T^2}$ (P)

so that, rearranging, we obtain the first claim. Using the fact, by Lemma 2.8, that;

$ln(Q(T_2)) = -\frac{\Delta G^{\circ}(T_2)}{RT_2}$

$ln(Q(T_1)) = -\frac{\Delta G^{\circ}(T_1)}{RT_1}$

we obtain, substituting into (P), canceling R, and performing the integration, if ΔH° is temperature independent, that;

$\frac{\Delta G^\circ(T_2)}{T_2} - \frac{\Delta G^\circ(T_1)}{T_1} = -\int_{T_1}^{T_2} \frac{\Delta H^\circ}{T^2} = \Delta H^\circ(\frac{1}{T_2} - \frac{1}{T_1})$ (Q)

For the fifth claim, rearrange (Q). If D_c intersects the line $P = P^\circ$ at (T_1, P°), for the sixth $(\dagger\dagger\dagger)$ and seventh claims, we have, using Lemma 2.8 and the fact from Lemma 2.10 that $Q(T_1, P^\circ) = 1$;

$(\frac{\partial G}{\partial \xi})_{T_2,P} = \Delta G^\circ(T_2) + RT_2 ln(Q(T_2, P))$

$= (\frac{\partial G}{\partial \xi})_{T_1,P^\circ}$

$= \Delta G^\circ(T_1) + RT_1 ln(Q(T_1, P^\circ))$

$= \Delta G^\circ(T_1) = c$

so that, again rearranging, we obtain the result. Along D_c, we have, using Lemma 2.8, that;

$ln(Q) = \frac{c - \Delta G^\circ}{RT}$

so that, using the first part;

$\frac{dln(Q)}{dT} = \frac{d}{dT}(\frac{c - \Delta G^\circ}{RT})$

$= \frac{-c}{RT^2} + \frac{d}{dT}(\frac{-\Delta G^\circ}{RT})$

$= \frac{\Delta H^\circ - c}{RT^2}$

so that, performing the integration, using the fact that $Q(T_1, P^\circ) = 1$;

$ln(Q(T_2)) - ln(Q(T_1)) = ln(Q(T_2)) = \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^\circ - c}{T^2} dT$

We have that, by Lemma 2.8;

$ln(Q(T_2)) = \frac{c - \Delta G^\circ(T_2)}{RT_2}$

$ln(Q(T_1)) = 0$

so that;

$ln(Q(T_2)) = ln(Q(T_2)) - ln(Q(T_1))$

$= \frac{c-\Delta G^\circ(T_2)}{RT_2}$

$= \frac{\Delta G^\circ(T_1)-\Delta G^\circ(T_2)}{RT_2}$

$= \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^\circ - c}{T^2} dT$

$= \frac{-1}{R}(\Delta H^\circ - c)(\frac{1}{T_2} - \frac{1}{T_1})$

and rearranging;

$\frac{\Delta G^\circ(T_2)-\Delta G^\circ(T_1)}{T_2} = (\Delta H^\circ - c)(\frac{1}{T_2} - \frac{1}{T_1})$

$= (\Delta H^\circ - \Delta G^\circ(T_1))(\frac{1}{T_2} - \frac{1}{T_1})$

so that, rearranging again;

$\Delta G^\circ(T_1)(\frac{1}{T_1} + \frac{1}{T_2} - \frac{1}{T_2}) = \frac{\Delta G^\circ(T_1)}{T_1}$

$= \frac{\Delta G^\circ(T_2)}{T_2} - \Delta H^\circ(\frac{1}{T_2} - \frac{1}{T_1})$

to obtain;

$\Delta G^\circ(T_1) = \frac{T_1}{T_2}\Delta G^\circ(T_2) - \Delta H^\circ(\frac{T_1}{T_2} - 1)$

□

Lemma 2.12. *If there exists a component D_c, $c \in \mathcal{R}$, which projects onto a closed bounded subinterval I of the line $P = P^\circ$, not containing 0, and intersects $P = P^\circ$ at (T_1, P°), with $T_1 > 0$, then, for $T_2 \in I$, ΔG° is linear, with;*

$\Delta G^\circ(T_2) = T_2(\frac{(\Delta G^\circ(T_1)-\Delta H^\circ)}{T_1}) + \Delta H^\circ$

for $T_2 \in I$. If $\epsilon \neq 0$, we have that;

$(\frac{dG}{d\xi})_{T,P} = \lambda + \epsilon P + \beta T$

where $\{\lambda, \epsilon, \beta\} \subset \mathcal{R}$ *and* $\{\beta, \epsilon\}$ *can be effectively determined, and we have that the activity coefficient is given by;*

$$Q(T_2, P') = e^{\frac{\epsilon(P' - P'^{\circ})}{RT_2}}$$

and the dynamic equilibrium paths are linear, given by;

$$P' = P'^{\circ} + \frac{RT_2 ln(c)}{\epsilon}$$

for $c \in \mathcal{R}_{\geq 0}$*, see Definition 2.1, while the quasi-chemical equilibrium paths are given by;*

$$\lambda + \epsilon P' + \beta T_2 = c$$

for $c \in \mathcal{R}$*.*

If $\epsilon = 0$*;*

$$(\frac{dG}{d\xi})_{T,P} = \lambda + \beta T + \sigma ln(T)$$

where $\{\lambda, \beta, \sigma\} \subset \mathcal{R}$*, and* $\{\beta, \sigma\}$ *can be effectively determined. For every* $T_1 > 0$*, there exists a straight line feasible chemical path* γ *with* $pr_{12}(\gamma) \subset (T = T_1)$*, which is both a dynamic and quasi-chemical equilibrium path, and* $Q(T, P) = 1$*.*

Proof. For the first claim, by Lemma 2.11, we have that;

$$\Delta G^{\circ}(T_2) = \frac{T_2}{T_1}\Delta G^{\circ}(T_1) - \Delta H^{\circ}(\frac{T_2}{T_1} - 1)$$

$$= T_2(\frac{(\Delta G^{\circ}(T_1) - \Delta H^{\circ})}{T_1}) + \Delta H^{\circ}$$

For the next claim, by Lemma 2.10 and the proof of Lemma 2.11, we have that;

$$(\frac{\partial(\frac{dG}{d\xi})_{T,P}}{\partial T})_P = (\frac{\partial(\sum_{i=1}^{c} \nu_i \mu_i)}{\partial T})_P$$

$$= \sum_{i=1}^{c} \nu_i (\frac{\partial \mu_i}{\partial T})_P$$

$$= \sum_{i=1}^{c} \nu_i (\frac{\partial \mu_i}{\partial T})_{P,n}$$

$= -\sum_{i=1}^{c} \nu_i \overline{S}_{m,i}$ $(*)$

To compute $\overline{S}_{m,i}$, we have by the first law of thermodynamics;

$dQ = dU + dL = dU + pdV$

where L is the work done by the system, see [5]. We have that $\Delta H_{mix} = \Delta V_{mix} = 0$ for an ideal solution, and $\Delta U_{mix} = \Delta H_{mix} + P\Delta V_{mix} = 0$, that is the internal energy $U_{mix} = \sum_{i=1}^{c} U_i$ is the sum of the internal energy of its components. We assume that component i is in thermal equilibrium T with an ideal gas at pressures (P, P_i^*). Then at constant (T, P, P_i^*), we have that;

$dG_{i,liq} = dU_{i,liq} + PdV_{i,liq} - TdS_{i,liq}$

$= -dG_{i,gas} = -dU_{i,gas} - P_i^* dV_{i,gas} + TdS_{i,gas}$

$= dH_{i,liq} - TdS_{i,liq} = -dH_{i,gas} + TdS_{i,gas}$

so that;

$d(H_{i,liq} + H_{i,gas}) = TdS_{i,liq} + TdS_{i,gas}$

and;

$dU_{i,liq} + PdV_{i,liq} + dU_{i,gas} + P_i^* dV_{i,gas} = d(H_{i,liq} + H_{i,gas})$

Integrating between the initial and final states of no evaporation and complete evaporation, we obtain that;

$-U_{i,liq} - PV_{i,liq} + U_{i,gas} + P_i^* V_{i,gas} = H_{i,gas} - H_{i,liq} = \Delta H_{i,vap}$

so that, rearranging;

$U_{i,liq}(T, P, n_i) = U_{i,gas} - \Delta H_{i,vap} - PV_{i,liq} + P_i^* V_{i,gas}$

It follows, as $V_{mix} = 0$ for an ideal solution, $\Delta U_{mix} = 0$ for a mixture of ideal gas, using the ideal gas law $PV = n_i RT$, for the components,

and the calculation of internal energy for an ideal gas,([1]);

$$U_{mix,liq}(T,P,n_1,\ldots,n_c) = \sum_{i=1}^{c} U_{i,liq}(T,P,n_i)$$

$$= \sum_{i=1}^{c} U_{i,gas} - \sum_{i=1}^{c} \Delta H_{i,vap} - P\sum_{i=1}^{c} V_{i,liq} + \sum_{i=1}^{c} P_i^* V_{i,gas}$$

$$= U_{mix,gas} - \sum_{i=1}^{c} \Delta H_{m,i,vap} n_i - PV_{liq} + \sum_{i=1}^{c} P_i^* \frac{n_i RT}{P_i^*}$$

$$= \sum_{i=1}^{c} \frac{3n_i RT}{2} - \sum_{i=1}^{c} \Delta H_{m,i,vap} n_i - PV_{liq} + \sum_{i=1}^{c} n_i RT$$

$$= \sum_{i=1}^{c} \frac{5n_i RT}{2} - \sum_{i=1}^{c} \Delta H_{m,i,vap} n_i - PV_{liq}$$

$$dU_{mix,liq} = \sum_{i=1}^{c} \frac{5RT}{2} dn_i + \sum_{i=1}^{c} \frac{5n_i R}{2} dT - \sum_{i=1}^{c} \Delta H_{m,i,vap} dn_i - V_{liq} dP$$

$$-PdV_{liq}$$

$$dQ_{mix,liq} = dU_{mix,liq} + PdV_{liq}$$

$$= \sum_{i=1}^{c} \frac{5RT}{2} dn_i + \sum_{i=1}^{c} \frac{5n_i R}{2} dT - \sum_{i=1}^{c} \Delta H_{m,i,vap} dn_i - V_{liq} dP$$

$$\frac{dQ_{mix,liq}}{T} = \sum_{i=1}^{c} \frac{5R}{2} dn_i + \sum_{i=1}^{c} \frac{5n_i R}{2} \frac{dT}{T} - \sum_{i=1}^{c} \Delta H_{m,i,vap} \frac{dn_i}{T} - V_{liq} \frac{dP}{T}$$

It follows that;

$$\overline{S}_{m,i} = \int_{\Delta n_i = 1} \left(\frac{dQ}{T}\right)_{n',T,P}, \ ([2])$$

---

[1] If the components are monatomic with 3 degrees of freedom, we can use the formula $U_{i,gas} = \frac{3n_i RT}{2}$. This can be derived using either the kinetic theory exactly or thermodynamically. Otherwise, we have to use the more general formula $U_{i,gas} = \frac{f_i n_i RT}{2}$ where f_i is the number of degrees of freedom. This is a slight approximation and effects the value of the constant β.

[2] Technically, we cannot apply the first two laws of thermodynamics to open systems. If this were the case, we have, by Lemma 2.5, that $dG = -SdT + VdP + \sum_{i=1}^{c} \mu_i dn_i$, (A), and, by the definition of enthalpy in Definition 2.1, that;

$$dH = d(U + PV)$$

$$= dU + PdV + VdP \ (\dagger)$$

$$= d(G + TS)$$

$$= dG + TdS + SdT \ (\dagger\dagger)$$

We then have that, using the second law $dS = \frac{dQ}{T}$, and the first law of thermodynamics, $dQ = dU + pdV$;

$$dG + SdT - VdP = ((dH - TdS - SdT) + SdT - VdP)$$

$$= (dH - TdS - VdP)$$

$$= (dH - dQ - VdP)$$

$$= (dU + PdV + VdP) - dQ - VdP)$$

$$= (dU + PdV - dQ)$$

$$= ((dQ - PdV) + PdV - dQ)$$

$$= 0$$

so that from (A), $\sum_{i=1}^{c} \mu_i dn_i = 0$, which is not the case, if we vary the molar amounts n_i.

Instead, we can follow the method of [5], and define entropy in the usual way, by keeping the molar amounts fixed (which would entail changing the molar amounts by hand as the reaction progresses). Similarly, we can apply the first law of thermodynamics in this situation. By the above, we have that;

$$U_{liq} = \sum_{i=1}^{c} \frac{5n_i RT}{2} - \sum_{i=1}^{c} \Delta H_{m,i,vap} n_i - PV_{liq}$$

$$V_{liq} = \sum_{i=1}^{c} n_i V_{m,i}$$

so that;

$$U_{liq} = \sum_{i=1}^{c} n_i [\frac{5RT}{2} - \Delta H_{m,i,vap} - PV_{m.i}]$$

This agrees with the approximation given in [5] for dilute solutions;

$$U_{liq} = \sum_{i=1}^{c} n_i u_i(T, P)$$

$$V_{liq} = \sum_{i=1}^{c} n_i v_i(T, P)$$

so that $u_i(T, P) \simeq \frac{5RT}{2} - \Delta H_{m,i,vap} - PV_{m.i}$, $v_i(T, P) \simeq V_{m,i}$

Keeping molar amounts fixed, and applying the first two laws of thermodynamics;

$$dS = \frac{dU_{liq} + PdV_{liq}}{T}$$

$$= \sum_{i=1}^{c} n_i (\frac{du_i + Pdv_i}{T})$$

$= \sum_{i=1}^{c} n_i ds_i$

where $du_i \simeq \frac{5RdT}{2}$, as $V_{m,i}$ is small, and $dv_i \simeq 0$.

$\frac{du_i + Pdv_i}{T} = ds_i \simeq \frac{5RdT}{2T}$

and integrating;

$s_i(T,P) \simeq \int \frac{5RdT}{2T} = \frac{5Rln(T)}{2} + c(n_1, \ldots, n_c)$

so that;

$S \simeq \sum_{i=1}^{c} \frac{5Rln(T)n_i}{2} + d((n_1, \ldots, n_c)\ (BB)$

Fermi claims in [5] that;

$d((n_1, \ldots, n_c) \simeq -R \sum_{i=1}^{c} n_i log(x_i)$

where $x_i = \frac{n_i}{n}$, $n = \sum_{i=1}^{c} n_i \simeq n_1$

(Presumably if we subtract the constant $\Delta S_{vap} = \frac{\Delta H_{vap}}{T_{vap}}$, we obtain a formula for the entropy of a dilute solution;

$S \simeq \sum_{i=1}^{c} n_i (C_{p_i} ln(T) - Rln(p) + a_i + Rln(R)) - R \sum_{i=1}^{c} n_i log(x_i) - \frac{\Delta H_{vap}}{T_{vap}}$

see later calculation, but we need to change Fermi's gas entropy calculation if we can't assume a mixture of ideal gases. It's not clear we can apply Fermi's calculation here, as you cannot have an ideal, dilute solution)

It follows that;

$\overline{S}_{m,i} = (\frac{\partial S}{\partial n_i})_{T,P,n'} \simeq \frac{5Rln(T)}{2} - R(log(x_i) + 1 - \sum_{j=1}^{c} x_j)$

$= \frac{5Rln(T)}{2} - Rlog(x_i)$

$\frac{\partial}{\partial T}((\frac{\partial G}{\partial \xi})|_{(T,P)}) = -\sum_{i=1}^{c} \nu_i \overline{S}_{m,i} \simeq -(\sum_{i=1}^{c} \nu_i) \frac{5Rln(T)}{2} + R \sum_{i=1}^{c} \nu_i log(x_i)$

$= -(\sum_{i=1}^{c} \nu_i) \frac{5Rln(T)}{2} + Rlog(Q)$

By the proof in the main text, $(\frac{\partial G}{\partial \xi})|_{(T,P)} = \epsilon P + \alpha(T)$, so we have that, including error terms for Q;

$Q(T,P) = e^{\frac{(\frac{\partial G}{\partial \xi})|_{(T,P)} - (\frac{\partial G}{\partial \xi})|_{(T,P^\circ)} - \epsilon(T,P)}{RT}}$

$= e^{\frac{\epsilon P + \alpha(T) - \epsilon P^\circ - \alpha(T) - \epsilon(T,P)}{RT}}$

$= e^{\frac{\epsilon(P-P^\circ)}{RT}} \prod_{i=1}^{c} x_i^{\nu_i}(T, P^\circ)$

$\simeq e^{\frac{\epsilon(P-P^\circ)}{RT}} \prod_{i=2}^{c} x_i^{\nu_i}(T, P^\circ)$ (for a dilute solution $x_1 \simeq 1$)

$\simeq e^{\frac{\epsilon(P-P^\circ)}{RT}} \prod_{i=2}^{c} (\frac{P^\circ}{k_i})^{\nu_i}$

$Rlog(Q) \simeq R \sum_{i=2}^{c} \nu_i log(\frac{P^\circ}{k_i})$

using the fact that $\epsilon \simeq 0$, and then, differentiating with respect to T;

$\alpha'(T) \simeq -(\sum_{i=1}^{c} \nu_i)\frac{5Rln(T)}{2} + R \sum_{i=2}^{c} \nu_i log(\frac{P^\circ}{k_i})$

$\alpha(T) \simeq \lambda + \beta T + \sigma T ln(T)$

where $\beta = (\sum_{i=1}^{c} \nu_i)\frac{5R}{2} + R \sum_{i=2}^{c} \nu_i log(\frac{P^\circ}{k_i})$, $\sigma = -(\sum_{i=1}^{c} \nu_i)\frac{5R}{2}$

$(\frac{\partial G}{\partial \xi})|_{(T,P)} \simeq \lambda + \epsilon P + \beta T + \sigma T ln(T)$

Equating cofficients, as in the main text, we have that $\sigma = 0$, so final result is unaffected, with different $\{\lambda, \beta\}$.

For the case of a dilute solution in which the solutes are gases dissolved in the mixture, obeying Henry's law without deviation,the solvent as substance 1, with $x_1 \simeq 1$, obeying Raoult's law;

$\frac{\partial(\frac{\partial G}{\partial \xi})|_{(T,P)}}{\partial P} = \sum_{i=1}^{c} \nu_i V_{m,i}$

$= \epsilon \simeq 0$

so that;

$(\frac{\partial G}{\partial \xi})|_{(T,P)} = \epsilon P + \alpha(T)$

so that, with error terms;

$Q = e^{\frac{\epsilon P + \alpha(T) - \epsilon P^\circ - \alpha(T) - \epsilon(T,P)}{RT}}$

$= \prod_{i=1}^{c} x_i^{\nu_i}(T, P^\circ) e^{\frac{\epsilon(P-P^\circ)}{RT}}$

$\simeq \prod_{i=2}^{c} x_i^{\nu_i}(T, P^\circ) e^{\frac{\epsilon(P-P^\circ)}{RT}}$

$= \prod_{i=2}^{c} (\frac{P^\circ}{k_i})^{\nu_i} e^{\frac{\epsilon(P-P^\circ)}{RT}}$

By Fermi's calculation, we have that vaporising the solution and calculating the entropy S_{gas}, assuming the vapour is ideal;

$S_{gas} = \sum_{i=1}^{c} n_i(C_{p_i} log(T) - Rlog(p_i) + a_i + Rlog(R))$

By Raoult's law for the solvent and Henry's law for the solutes, without error terms, $p_1 = p_1^* x_i$, where $log(p_1^*) = \frac{V_{m,1}P}{RT} \simeq 0$, $p_i = k_i x_i$, $2 \leq i \leq c$, $log(p_i) = log(k_i) + log(x_i)$, so that;

$S_{gas} \simeq n_1(C_{p_1} log(T) - Rlog(x_1) + a_1 + Rlog(R)) + \sum_{2 \leq i \leq c} n_i(C_{p_i} log(T)$

$-Rlog(x_i) - Rlog(k_i) + a_i + Rlog(R))$

$S_{liquid} \simeq n_1(C_{p_1} log(T) - Rlog(x_1) + a_1 + Rlog(R)) + \sum_{2 \leq i \leq c} n_i(C_{p_i} log(T)$

$-Rlog(x_i) - Rlog(k_i) + a_i + Rlog(R)) - \frac{\Delta H_{vap}}{T_{vap}}$

so that;

$S_{liquid} \simeq n_1(C_{p_1} log(T) - Rlog(x_1) + a_1 + Rlog(R)) + \sum_{2 \leq i \leq c} n_i(C_{p_i} log(T)$

$-Rlog(x_i) - Rlog(k_i) + a_i + Rlog(R)) - \sum_{i=1}^{c} n_i \frac{\Delta H_{vap,i,m}}{T_{vap}}$ (mixing correction?)

$S_{m,1} \simeq \frac{\partial S}{\partial n_1} = C_{p_1} log(T) - Rlog(x_1) + a_1 + Rlog(R) - \frac{\Delta H_{vap,i,m}}{T_{vap}}$

$S_{m,i} \simeq (C_{p_i} log(T) - Rlog(x_i) - Rlog(k_i) + a_i + Rlog(R)) - \frac{\Delta H_{vap,i,m}}{T_{vap}}$ $(2 \leq i \leq c)$

$\frac{\partial(\frac{\partial G}{\partial \xi})|_{(T,P)}}{\partial T} = -\sum_{i=1}^{c} \nu_i S_{m,i}$

$= -\sum_{1 \leq i \leq c} \nu_i C_{p_i} log(T) + \sum_{1 \leq i \leq c} \nu_i Rlog(x_i) - \sum_{1 \leq i \leq c} \nu_i a_i$

$-\sum_{1 \leq i \leq c} \nu_i Rlog(R) + \sum_{2 \leq i \leq c} \nu_i Rlog(k_i) + \sum_{1 \leq i \leq c} \nu_i \frac{\Delta H_{vap,i,m}}{T_{vap}}$

$= -\sum_{1 \leq i \leq c} \nu_i C_{p_i} log(T) + Rlog(Q) + K$

$\simeq -\sum_{1 \leq i \leq c} \nu_i C_{p_i} log(T) + K$

$\simeq \alpha'(T)$

where $K = (\sum_{1 \leq i \leq c} \nu_i)(-Rlog(R) + \frac{\Delta H_{vap,i,m}}{T_{vap}}) - \sum_{1 \leq i \leq c} \nu_i a_i$

$+ \sum_{2 \leq i \leq c} \nu_i (Rlog(k_i) + log(\frac{P^\circ}{k_i}))$

so that $\alpha(T) \simeq -\sum_{1 \leq i \leq c} \nu_i C_{p_i} T log(T) + \beta T + \lambda$

where $\beta = \sum_{1 \leq i \leq c} \nu_i C_{p_i} + K$

It follows that;

$(\frac{\partial G}{\partial \xi})|_{(T,P)} = \epsilon P - \sum_{1 \leq i \leq c} \nu_i C_{p_i} T log(T) + \beta T + \lambda$

$= \frac{5R}{2} - \frac{\Delta H_{m,i,vap}}{T}$

So that, from $(**)$;

$(\frac{\partial(\frac{dG}{d\xi})_{T,P}}{\partial T})_P = -\sum_{i=1}^{c} \nu_i(\frac{5R}{2} - \frac{\Delta H_{m,i,vap}}{T})$

$= -\frac{5R}{2}(\sum_{i=1}^{c} \nu_i) + \frac{1}{T}(\sum_{i=1}^{c} \nu_i \Delta H_{m,i,vap})$ $(***)$

and we assume that $\Delta H_{m,i,vap}$ is independent of (T, P). From $(***)$, which is uniform P, we see that $(\frac{dG}{d\xi})_{T,P}$ is of the form $\alpha(P) + \beta T + \sigma ln(T)$, (B), where $\{\beta, \sigma\} \subset \mathcal{R}$, and, assuming that $(\frac{dG}{d\xi})_{T,P}$ is differentiable, $\alpha \in C^1(\mathcal{R})$. By a similar calculation, we have that;

$(\frac{\partial(\frac{dG}{d\xi})_{T,P}}{\partial P})_T = (\frac{\partial(\sum_{i=1}^{c} \nu_i \mu_i)}{\partial P})_T$

$= \sum_{i=1}^{c} \nu_i (\frac{\partial \mu_i}{\partial P})_T$

$= \sum_{i=1}^{c} \nu_i (\frac{\partial \mu_i}{\partial P})_{T,n}$

$= \sum_{i=1}^{c} \nu_i (\frac{\partial V}{\partial n_i})_{T,P,n'}$

$= \sum_{i=1}^{c} \nu_i \overline{V}_{m,i}$

$= \sum_{i=1}^{c} \nu_i \frac{N_A m_i}{\kappa_i(T,P)}$ (A)

where κ_i is the density of substance i, m_i is the molecular mass, and we assume that $\overline{V}_{m,i}$ is independent of (T, P). We have, from (A, B), that;

$(\frac{\partial(\frac{dG}{d\xi})_{T,P}}{\partial P})_T = \epsilon = \alpha'(P)$ (AA)

---

where, equating coefficients, as in the main text;

$-\sum_{1 \leq i \leq c} \nu_i C_{p_i} \simeq 0$

$\lambda + \epsilon P^\circ = \Delta H^\circ$

$\beta = \frac{\Delta G^\circ(T) - \Delta H^\circ}{T}$

where $\epsilon = \sum_{i=1}^{c} \nu_i \overline{V}_{m,i}$, so that;

$\alpha(P) = \lambda + \epsilon P$

and;

$(\frac{dG}{d\xi})_{T,P}$ is of the form;

$\alpha(P) + \beta T + \sigma ln(T)$

$= \lambda + \epsilon P + \beta T + \sigma ln(T)$ (D)

where $\{\beta, \epsilon, \lambda, \sigma\} \subset \mathcal{R}$.

If $\epsilon = 0$, then $(\frac{dG}{d\xi})_{T,P}$ is independent of P, and the components D_c are all straight line paths. In this case, if D_c intersects the line $P = P^\circ$ at (T_1, P°), then, for all $P > 0$;

$c = \Delta G^\circ(T_1) + RT_1 ln(Q(T_1, P)$

$= \Delta G^\circ(T_1)$

implies that $RT_1 ln(Q(T_1, P) = 0$, so that $Q(T_1, P) = 1$ and, by Lemmas 2.17 and 2.19, there exists a straight line feasible chemical path γ with $pr_{12}(\gamma) \subset (T = T_1)$, which is both a dynamic and quasi-chemical equilibrium path. From (D), we have that;

$(\frac{dG}{d\xi})_{T,P} = \lambda + \beta T + \sigma ln(T)$

We have that, for any $T_1 > 0$, we can find $c \in \mathcal{R}$ with $\lambda + \beta T_1 + \sigma ln(T_1) = c$, so that D_c defines a component straight line path passing through (T_1, P°). Then we can apply the previous result.

If $\epsilon \neq 0$, there exists a component D_c given by;

$\lambda + \epsilon P + \beta T + \sigma ln(T) = c$

projecting generically onto the line $P = P^0$ and, by the first part, ΔG° is linear, with;

$\Delta G^{\circ}(T_2) = T_2(\frac{(\Delta G^{\circ}(T_1) - \Delta H^{\circ})}{T_1}) + \Delta H^{\circ}$

for an intersection at (T_1, P°). We also have, using (D), that;

$\Delta G^{\circ}(T_2) = (\frac{\partial G}{\partial \xi})_{T,P}(T_2, P^{\circ})$

$= \lambda + \epsilon P^{\circ} + \beta T_2 + \sigma ln(T_2)$

so that, equating coefficients;

$\sigma = 0$

$\lambda + \epsilon P^{\circ} = \Delta H^{\circ}$

$\beta = \frac{(\Delta G^{\circ}(T_1) - \Delta H^{\circ})}{T_1}$

$\Delta G^{\circ}(T_1) = \beta T_1 + \Delta H^{\circ}$

$\Delta G^{\circ}(T_2) = \beta T_2 + \Delta H^{\circ}$

We can then, using Lemma 2.8, obtain a formula for the activity coefficient;

$Q(T_2, P') = e^{\frac{((\frac{\partial G}{\partial \xi})_{T,P}|_{T_2,P'} - \Delta G^{\circ}(T_2))}{RT_2}}$

$e^{\frac{(\Delta H^{\circ} - \epsilon P'^{\circ} + \epsilon P' + \beta T_2 - (\beta T_2 + \Delta H^{\circ}))}{RT_2}}$

$= e^{\frac{\epsilon(P' - P'^{\circ})}{RT_2}}$ (W)

as required. The claim about the coefficients being determined is clear from the proof. The determination of the dynamical and quasi-chemical equilibrium lines, see Definitions 2.1 and Lemma 2.20, follows from a simple rearrangement of the formulas $Q(T_1, P') = c$, for some $c \in \mathcal{R}_{\geq 0}$, using (W), and $(\frac{dG}{d\xi})_{T,P} = c$, for some $c \in \mathcal{R}$, using (D), with $\sigma = 0$.

□

Lemma 2.13. *With notation as in Lemma 2.12, if $\epsilon = 0$, then if either;*

(i). $\beta > 0, \sigma > 0$

$(ii).\ \beta < 0, \sigma < 0$

$(iii).\ \beta > 0, \sigma < 0, \lambda - \sigma + \sigma ln(\frac{-\sigma}{\beta}) \leq 0$

$(iv).\ \beta < 0, \sigma > 0, \lambda - \sigma + \sigma ln(\frac{-\sigma}{\beta}) \geq 0$

we can always find $T_0 > 0$*, defined as the solution to* $\lambda + \beta T + \sigma ln(T) = 0$*, such that* $T = T_0$ *defines a chemical equilibrium line.*

Proof. By the proof of Lemma 2.12, if T_0 is a solution to;

$\lambda + \beta T + \sigma ln(T) = 0\ (*)$

then $(\frac{\partial G}{\partial \xi})_{T,P}|_{T=T_0} = 0$

so that $T = T_0$ defines a chemical equilibrium line. By considering limits at ∞ and noting that the derivative $\beta + \frac{\sigma}{T}$ of $\lambda + \beta T + \sigma ln(T)$, is of a fixed sign in cases $(i), (ii)$, so that $\lambda + \beta T + \sigma ln(T)$ is monotonic, we can see there does exist a unique solution T_0 in cases $(i), (ii)$. In cases $(iii), (iv)$, computing limits at ∞ again, and noting that $\beta + \frac{\sigma}{T}$ is increasing/decreasing, we have that, if the minimum/maximum T_1 respectively of $\lambda + \beta T + \sigma ln(T)$, given by the solution to;

$\beta + \frac{\sigma}{T} = 0$

so that $T_1 = \frac{-\sigma}{\beta}$, then, in case (iii), if;

$\lambda + \beta(T_1) + \sigma ln(T_1) < 0$

iff $\lambda - \sigma + \sigma ln(\frac{-\sigma}{\beta}) < 0$

there exist two possible solutions T_0, with a unique solution if equality holds. Similarly, then, in case (iv), if;

$\lambda - \sigma + \sigma ln(\frac{-\sigma}{\beta}) > 0$

there exist at least two possible solutions T_0, with again a unique solution if equality holds.

□

Lemma 2.14. *If* $\epsilon = 0$*, we have, for all* $T_1 > 0$*, that;*

$(\frac{\partial G}{\partial \xi})_{T,P}|_{(T_1,P_1)} = (\frac{\partial G}{\partial \xi})_{T,P}|_{(T_1,P_1^\circ)}$

iff;

$E(T_1,P_1) = E(T_1,P_1^\circ) = E^\circ(T_1)$

where G is the Gibbs energy function for the charged and uncharged species.

Proof. By (†) of Lemma 2.7, we have that;

$(\frac{\partial G}{\partial \xi})_{T,P} = (\frac{\partial G_{chem'}}{\partial \xi})_{T,P} + 2EF \ (*)$

By Lemma 2.12, we have that $(\frac{\partial G_{chem'}}{\partial \xi})_{T,P}$ is independent of P, in particularly, we have that;

$(\frac{\partial G_{chem'}}{\partial \xi})_{T_1,P_1} = (\frac{\partial G_{chem'}}{\partial \xi})_{T_1,P_1^\circ} \ (**)$

so that, combining $(*), (**)$, we obtain the result. □

Lemma 2.15. *We have, for all $T_1 > 0, P_1 > 0$, that;*

$2F(E(T_1,P_1) - E^\circ(T_1)) = (\frac{\partial G}{\partial \xi})_{T,P}|_{(T_1,P_1)} - (\frac{\partial G}{\partial \xi})_{T,P}|_{(T_1,P_1^\circ)} - RT_1 ln(Q(T_1,P_1))$

Proof. Following the proof of Lemma 2.7, we have that;

$(\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1} = (\frac{\partial G_{chem'}}{\partial \xi})_{T,P}|_{T_1,P_1} + 2E(T_1,P_1)F \ (*)$

$2E^\circ(T_1)F = (\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1^\circ} - (\frac{\partial G_{chem'}}{\partial \xi})_{T,P}|_{T_1,P_1^\circ}$

$= (\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1^\circ} - \Delta G^\circ_{chem'}(T_1) \ (**)$

so from $(*), (**)$ and Lemma 2.8;

$2E(T_1,P_1)F = (\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1} - (\frac{\partial G_{chem'}}{\partial \xi})_{T,P}|_{T_1,P_1}$

$= (\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1} - (\Delta G^\circ_{chem'}(T_1) + RT_1 ln(Q_{chem'}(T_1,P_1)))$

$2E(T_1,P_1)F - 2E^\circ(T_1)F = (\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1} - (\Delta G^\circ_{chem'}(T_1) + RT_1 ln(Q_{chem'}(T_1,P_1)))$

$-((\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1^\circ} - \Delta G^\circ_{chem'}(T_1))$

$= (\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1} - ((\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1^\circ} - RT_1 ln(Q_{chem'}(T_1,P_1))$

□

Definition 2.16. *Ideal Solution*

We let pr_1 is the projection onto the first factor, pr_{12} be the projection onto the first two factors, in coordinates $(T,P,n_1,\ldots,n_c)$. We define a feasible chemical path $\gamma : [0,1] \to \mathcal{R}^{2+c}_{>0}$, such that if $n_i(t) = pr_{2+i}(t)$, for $1 \leq i \leq c$, then;

$\frac{n_i'}{\nu_i} = \frac{n_j'}{\nu_j}$, *for* $1 \leq i < j \leq c$

where $\{\nu_1,\ldots,\nu_c\}$ are the stoichiometric coefficients. If $n(t) = \sum_{i=1}^c n_i(t)$, and $x_i(t) = a_i(t) = \frac{n_i}{n}(t)$, then $Q(pr_{12}(\gamma(t))) = \prod_{i=1}^c a_i(t)^{\nu_i}$ and $\frac{n_{i,0}}{n_0} = f_i(pr_{12}(\gamma(0)))$, where $f_i = e^{\frac{\mu_i - \mu_i^\circ}{RT}}$, $1 \leq i \leq c$, see Section 14. Note that $n > 0$ and the x_i are well defined.

We define a chemical equilibrium path to be a feasible chemical path γ with the additional property that chemical equilibrium exists at $pr_{12}(\gamma(t))$, for $t \in [0,1]$. We define a quasi-chemical equilibrium path to be a feasible chemical path γ with the additional property that $(\frac{\partial G}{\partial \xi})_{T,P}|_{pr_{12}([0,1])}$ is constant. We define a dynamic equilibrium path to be a feasible chemical path γ with the additional property that $pr_{2+c}(\gamma)'(t) = 0$, for $1 \leq i \leq c$.

We define a straight line feasible path from (T,P°) to (T,P) to be a map $\gamma : [0,1] \to \mathcal{R}^{2+c}_{\geq 0}$ such that $pr_{12}\gamma(0) = (T,P^\circ)$, $pr_{12}\gamma(1) = (T,P)$, $pr_1(\gamma(t)) = T$. We say that a point (T,P) is a simple dynamic equilibrium point, if it lies on the locus $Q(T,P) = 1$.

Lemma 2.17. *In an ideal solution, a straight line chemical equilibrium path from (T,P°) to (T,P) is a dynamic equilibrium path. Every (T,P°) is a simple dynamic equilibrium point.*

Proof. By Lemma 2.10, and the definition of activities for an ideal solution, we have that;

$1 = Q(T,P) = \prod_{i=1}^c a_i^{\nu_i} = \prod_{i=1}^c x_i^{\nu_i}$ $(*)$

and $\frac{n_i'}{\nu_i} = \frac{n_j'}{\nu_j}$, for $1 \leq i,j \leq c$, $\sum_{i=1}^c n_i = n$

Using the relation $(*)$, differentiating and using the facts that, for $1 \leq i \leq c-1$;

$n_i' = \frac{\nu_i n_c'}{\nu_c}$, $n_i = \frac{\nu_i n_c}{\nu_c} + d_i$ (!)

we obtain that;

$(\prod_{i=1}^{c} x_i^{\nu_i})' = \sum_{i=1}^{c} \nu_i x_i^{\nu_i - 1} x_i' \prod_{j \neq i} x_j^{\nu_j}$

$= \sum_{i=1}^{c} \nu_i x_i^{\nu_i - 1} x_i' x_i^{-\nu_i}$

$= \sum_{i=1}^{c} \nu_i x_i^{-1} x_i'$

$= \sum_{i=1}^{c} \nu_i \frac{n}{n_i} \frac{(n_i' n - n_i n')}{n^2}$

$= \sum_{i=1}^{c} \nu_i (\frac{n_i'}{n_i} - \frac{n'}{n})$

$= \sum_{i=1}^{c-1} \frac{\nu_i^2 n_c'}{\nu_i n_c + \nu_c d_i} + \frac{\nu_c n_c'}{n_c} - \lambda(\frac{\sum_{i=1}^{c} n_i'}{\sum_{i=1}^{c} n_i})$

$= \sum_{i=1}^{c-1} \frac{\nu_i^2 n_c'}{\nu_i n_c + \nu_c d_i} + \frac{\nu_c n_c'}{n_c} - \lambda(\frac{(\sum_{i=1}^{c-1} \frac{\nu_i}{\nu_c} + 1) n_c'}{(\sum_{i=1}^{c-1} \frac{\nu_i}{\nu_c} + 1) n_c + \sum_{i=1}^{c-1} d_i})$

$= 0$ (B)

where $\lambda = \sum_{i=1}^{c} \nu_i$. If $\nu_c' \neq 0$, we obtain that;

$= \sum_{i=1}^{c-1} \frac{\nu_i^2}{\nu_i n_c + \nu_c d_i} + \frac{\nu_c}{n_c} - \lambda(\frac{(\sum_{i=1}^{c-1} \frac{\nu_i}{\nu_c} + 1)}{(\sum_{i=1}^{c-1} \frac{\nu_i}{\nu_c} + 1) n_c + \sum_{i=1}^{c-1} d_i}) = 0$

so that;

$\sum_{i=1}^{c-1} \nu_i^2 n_c (\alpha n_c + \beta) \prod_{j \neq i} (\nu_j n_c + \nu_c d_j) + \nu_c (\alpha n_c + \beta) \prod_{i=1}^{c-1} (\nu_i n_c + \nu_c d_i)$

$-\lambda n_c \prod_{i=1}^{c-1} (\nu_i n_c + \nu_c d_i) = 0$

where $\alpha = \sum_{i=1}^{c-1} \frac{\nu_i}{\nu_c} + 1$ and $\beta = \sum_{i=1}^{c-1} d_i$

which we can write in the form;

$\sum_{j=0}^{c} \gamma_j \nu_c^j = 0$

We have that;

$\gamma_c = \sum_{i=1}^{c-1} \nu_i^2 \alpha \prod_{j \neq i} \nu_j + \alpha \nu_c \prod_{i=1}^{c-1} \nu_i - \lambda \prod_{i=1}^{c-1} \nu_i$

$= \alpha\delta \sum_{i=1}^{c-1} \nu_i + \alpha\delta\nu_c - \lambda\delta$

$= \delta(\alpha(\sum_{i=1}^{c} \nu_i) - \lambda)$

$= \delta\lambda(\alpha - 1)$

Noting that $\delta \neq 0$ and $\alpha - 1 = \sum_{i=1}^{c-1} \frac{\nu_i}{\nu_c}$, we have that $\gamma_c \neq 0$ iff $\sum_{i=1}^{c-1} \nu_i \neq 0$ and $\sum_{i=1}^{c} \nu_i \neq 0$. In this case, we obtain a nontrivial polynomial relation $p(n_c) = 0$, so that, by continuity and discreteness of roots, n_c is a constant and $n_c' = 0$. By the connecting relations (!), we obtain that $n_j' = 0$ as well, for $\leq j \leq c - 1$.

If $\sum_{i=1}^{c} \nu_i = 0$ (G) then $\sum_{i=1}^{c-1} \nu_i \neq 0$, and, we have, from $(*)$, that;

$\prod_{i=1}^{c} n_i^{\nu_i} = n^{\sum_{i=1}^{c} \nu_i} = 1$ (A)

and, following the calculation (B), we obtain;

$\sum_{i=1}^{c-1} \frac{\nu_i^2 n_c'}{\nu_i n_c + \nu_c d_i} + \frac{\nu_c n_c'}{n_c} = 0$

so that, if $n_c' \neq 0$;

$\sum_{i=1}^{c-1} \frac{\nu_i^2}{\nu_i n_c + \nu_c d_i} + \frac{\nu_c}{n_c} = 0$

and, differentiating k times, for $k \geq 0$, cancelling n_c' if $n_c' \neq 0$, and using the chain rule, we obtain the relations;

$\sum_{i=1}^{c-1} \frac{\nu_i^{k+2}}{(\nu_i n_c + \nu_c d_i)^{k+1}} + \frac{\nu_c}{n_c^{k+1}} = 0$

Let $g_i = \frac{1}{\nu_i + \frac{\nu_c d_i}{n_c}} = \frac{n_c}{\nu_c n_i} < 0$, for $1 \leq i \leq c - 1$. Then, for $k \geq 0$;

$\sum_{i=1}^{c-1} \nu_i^{k+2} g_i^{k+1} + \nu_c = \sum_{i=1}^{c-1} \nu_i (\nu_i g_i)^{k+1} + \nu_c$

$= 0$ (E)

If $g_i = -1$, then;

$\frac{n_c}{\nu_c n_i} = \frac{n_c}{\nu_c(\frac{\nu_i n_c}{\nu_c} + d_i)} = \frac{n_c}{\nu_i n_c + \nu_c d_i} = -1$

so that;

$n_c = -(\nu_i n_c + \nu_c d_i)$

$(1 + \nu_i)n_c = \nu_c d_i$

Then if $n'_c \neq 0$, we must have that $\nu_i = -1$, $d_i = 0$. Rescaling each ν_i by a factor of 2, we still have the conditions $(*)$, (E),(G), so we can assume that $|\nu_i| \geq 2$, which is a contradiction. Hence, we can assume that $|g_i| \neq 1$, for $1 \leq i \leq c-1$, so that taking the limit as $k \to \infty$, with k even, so that $\nu_i^{k+2} > 0$, $g_i^{k+1} < 0$, for $1 \leq i \leq c-1$, we obtain a contradiction, and conclude that $n'_c = 0$, and $n'_i = 0$, for $1 \leq i \leq c-1$.

If for every $c-1$ element subset $I_j \subset \{\nu_1, \dots \nu_c\}$, $1 \leq j \leq c$, we have that $\sum_{i \in I_j} \nu_i = 0$, then clearly;

$\sum_{1 \leq i \leq c} \nu_i = \sum_{i \in I_j} \nu_i + \nu_j$

$= \nu_j$ for $1 \leq j \leq c$

which we can exclude. It follows that there exists some j_0, with $1 \leq j_0 \leq c$, such that $\sum_{i \in I_{j_0}} \nu_i \neq 0$. Using n_{j_0} as the pivot and following the above proof, replacing n_c by n_{j_0}, we can, without loss of generality, assume that $\sum_{i=1}^{c-1} \nu_i \neq 0$, and the proof is complete.

The second claim follows from the fact in Lemma 2.10 that $Q(T, P^\circ) = 1$.

□

Definition 2.18. *For $c \in \mathcal{R}_{>0}$, we define $C_c \subset \mathcal{R}^2$ to be the zero locus of $Q(T,P) - c$. We define $D \subset \mathcal{R}^2$ to be the condition of chemical equilibrium. We define D_c to be the zero locus of $(\frac{\partial G}{\partial \xi})_{T,P} - c = 0$.*

Lemma 2.19. *For every smooth curve $W \subset \mathcal{R}^2$, there exists a locally feasible path $\gamma : [0,1] \to \mathcal{R}^{2+c}$ with $pr_{12}(\gamma) \subset W$.*

Proof. As W is smooth, we can choose a local parametrisation $\delta : [0,1] \to W$. Let $\epsilon(t) = Q(\delta(t)) > 0$ and $w = \sum_{i=1}^{c} \nu_i$. Without loss of generality, we can assume that $pr_{12}(\gamma(0)) = (T_0, P_0)$, see Section 14. We have that;

$\prod_{i=1}^{c} x_i^{\nu_i}(t) = \epsilon(t)$ $(\dagger)$

iff $\prod_{i=1}^{c} n_i^{\nu_i}(t) = \epsilon(t) n^{\sum_{i=1}^{c} \nu_i}(t)$

iff $\prod_{i=1}^{c-1} n_i^{\nu_i}(t) n_c^{\nu_c}(t) = \epsilon(t)(\sum_{i=1}^{c} n_i)^{\sum_{i=1}^{c} \nu_i}(t)$

iff $\prod_{i=1}^{c-1} (\frac{\nu_i}{\nu_c} n_c + d_i)^{\nu_i}(t) n_c^{\nu_c}(t) = \epsilon(t)(\sum_{i=1}^{c} n_i)^{\sum_{i=1}^{c} \nu_i}(t)$

iff $\prod_{i=1}^{c-1} (\frac{\nu_i}{\nu_c} n_c + d_i)^{\nu_i}(t) n_c^{\nu_c}(t) = \epsilon(t)((\sum_{i=1}^{c-1} \frac{\nu_i}{\nu_c} + 1) n_c + \sum_{i=1}^{c-1} d_i)^{w}(t)$

Let $d_i > 0$, for $1 \leq i \leq c-1$, then;

$\prod_{i=1}^{c} x_i^{\nu_i}(t) = \epsilon(t)$

iff $\prod_{i=1}^{c-1} (\frac{\nu_i}{\nu_c} n_c + d_i)^{\nu_i}(t) n_c^{\nu_c}(t) = \epsilon(t)((\sum_{i=1}^{c-1} \frac{\nu_i}{\nu_c} + 1) n_c + \sigma)^{w}(t)$

iff $\prod_{i=1}^{c-1} (\frac{\nu_i}{\nu_c} n_c + d_i)^{\nu_i}(t) n_c^{\nu_c}(t) = \epsilon(t)(\frac{w}{\nu_c} n_c + \sigma)^{w}(t)$

where $\sigma = \sum_{i=1}^{c-1} d_i > 0$. Assume that $w > 0$, then we have that;

$\prod_{i=1}^{c} x_i^{\nu_i}(t) = \epsilon(t)$

iff $\prod_{i=1}^{p} (\frac{\nu_i}{\nu_c} n_c + d_i)^{\nu_i} = \epsilon(t)(\frac{w}{\nu_c} n_c + \sigma)^{w}(t) n_c^{-\nu_c} \prod_{i=p+1}^{c-1} (\frac{\nu_i}{\nu_c} n_c + d_i)^{-\nu_i}$

iff $\prod_{i=1}^{p} (\frac{\nu_i}{\nu_c})^{\nu_i} n_c^{\kappa} + r(n_c) = \epsilon(t)[(\frac{w}{\nu_c})^{w} \prod_{i=p+1}^{c-1} (\frac{\nu_i}{\nu_c})^{-\nu_i} n_c^{w-\nu_c-\lambda} + s(n_c)]$

iff $\prod_{i=1}^{p} (\frac{\nu_i}{\nu_c})^{\nu_i} n_c^{\kappa} + r(n_c) = \epsilon(t)[(\frac{w}{\nu_c})^{w} \prod_{i=p+1}^{c-1} (\frac{\nu_i}{\nu_c})^{-\nu_i} n_c^{\kappa} + s(n_c)]$

iff $\alpha n_c^{\kappa} + r(n_c) = \epsilon(t)(\beta n_c^{\kappa} + s(n_c))$ $(\dagger\dagger\dagger)$

where $\alpha = \prod_{i=1}^{p} (\frac{\nu_i}{\nu_c})^{\nu_i} \neq 0$, $\beta = (\frac{w}{\nu_c})^{w} \prod_{i=p+1}^{c-1} (\frac{\nu_i}{\nu_c})^{-\nu_i} \neq 0$, $\lambda = \sum_{i=p+1}^{c-1} \nu_i$, $\{r, s\} \subset \mathcal{R}[x]$ have degree less than κ, $r(0) = \prod_{i=1}^{p} d_i > 0$, $s(0) = 0$, as divisible by $x^{-\nu_c}$. Dividing $(\dagger\dagger\dagger)$ by $n_c^{\kappa} > 0$, we obtain;

$\alpha + r_1(\frac{1}{n_c}) = \epsilon(t)(\beta + s_1(\frac{1}{n_c}))$ (C)

where $\{r_1, s_1\} \subset \mathcal{R}[x]$ have degree κ, with $r_1(0) = s_1(0) = 0$, $deg(r_1) = \kappa$ and $c_\kappa = r(0) = \prod_{i=1}^{p} d_i > 0$ where $r_1 = \sum_{j=0}^{\kappa} c_j x^j$, $deg(s_1) \leq \kappa + \nu_c < \kappa$, so that $lim_{x \to \infty} \frac{\alpha + r_1(x)}{\beta + s_1(x)} = \infty$.

Let $v(x) = \alpha x^\kappa + r(x)$, $w(x) = \beta x^\kappa + s(x)$. Then, the roots v_i of $r(x)$, $1 \leq i \leq p$, are given by $v_i = -\frac{d_i \nu_c}{\nu_i} > 0$, while the roots w_i of $w(x)$ are given by $w_0 = 0$, $w_i = \frac{-d_i \nu_c}{\nu_i} < 0$, $p+1 \leq i \leq c-1$ and $w_c = \frac{-\sigma \nu_c}{w}$. If $\nu_i = w$, for $1 \leq i \leq p$, it would follow that $w > \sum_{i=1}^{p} \nu_i = pw$, which is a contradiction, as $p \geq 1$. It follows that we can choose i_0 with $1 \leq i_0 \leq p$ such that $\frac{-\nu_c}{\nu_{i_0}} \neq \frac{-\nu_c}{w}$ and $\frac{-\nu_c d_{i_0}}{\nu_{i_0}} \neq \frac{-\nu_c d_{i_0}}{w}$,([3]). Dividing by x^κ doesn't effect the positive roots v_i, $1 \leq i \leq p$ of $\frac{r(x)}{x^\kappa} = \alpha + r_1(\frac{1}{x})$, and the positive roots of $\alpha + r_1(x)$, are the positive reciprocals $v_i' = \frac{1}{v_i}$, $1 \leq i \leq p$. As $lim_{x \to \infty} \frac{\alpha + r_1(x)}{\beta + s_1(x)} = \infty$ and $\epsilon(0) > 0$, we can choose v_0 with $q(v_0) = \epsilon(0)$ and $v_0 > v_i'$, for $1 \leq i \leq p$, where $q(x) = \frac{\alpha + r_1(x)}{\beta + s_i(x)}$. Then $\frac{1}{v_0} < \frac{1}{v_i'} = v_i$, for $1 \leq i \leq p$, and as $\frac{\nu_i}{\nu_c} < 0$, $\frac{\nu_i}{\nu_c}\frac{1}{v_0} > \frac{\nu_i}{\nu_c} v_i$, $\frac{\nu_i}{\nu_c}\frac{1}{v_0} + d_i > \frac{\nu_i}{\nu_c} v_i + d_i = 0$, for $1 \leq i \leq p$. In particularly, as $n_c(0) = \frac{1}{v_0}$, we have, by the linking relations, that $n_i(0) = \frac{\nu_i}{\nu_c} n_c(0) + d_i = \frac{\nu_i}{\nu_c}\frac{1}{v_0} + d_i > 0$, for $1 \leq i \leq p$. Moreover, as $\frac{\nu_i}{\nu_c} > 0$, for $i+1 \leq i \leq c-1$, and $\frac{1}{v_0} > 0$, we have that $n_i(0) = \frac{\nu_i}{\nu_c} n_c(0) + d_i = \frac{\nu_i}{\nu_c}\frac{1}{v_0} + d_i > 0$ as well, for $i+1 \leq i \leq p-1$, (D)

By (C), we have that $q(\frac{1}{n_c}) = \epsilon(t)$ and, by the above construction, it follows that $q(v_0) = \epsilon(0)$. Consider the real algebraic curve defined by $\theta(x,y) = q(x) - y - \epsilon(0)$, so that $\theta(v_0, 0) = 0$. Computing the differential $(q'(x), -1)$, if $q'(v_0) \neq 0$, we see that the projection pr_y is unramified at $(v_0, 0)$, so that we can apply the inverse function theorem, see [12], to obtain a real branch $\gamma(y)$ with $\gamma(0) = v_0$ and;

$$\theta(\gamma(y), y) = q(\gamma(y)) - y - \epsilon(0) = 0$$

[3]As n_c is mobile, the conditions that $n_{i,0} = d_i + \frac{\nu_i}{\nu_c} n_{c,0}$, $1 \leq i \leq c-1$, (B), together with the requirement that $\overline{n}_0 = (n_{1,0}, \ldots, n_{c,0})$ lies in $Ker(M) \cap \mathcal{R}^c_{>0}$, see Section 14, places a 1 dimensional restriction on the tuple $(d_1, \ldots d_{c-1})$, defined as $pr_{c-1}(W)$, where $W = V \cap g^{-1}(Ker(M))$, $V = \{(d_1, \ldots d_{c-1}, n_{c,0}(d_1, \ldots d_{c-1})) : (d_1, \ldots d_{c-1}) \in \mathcal{R}^{c-1}\}$, and $g(x_1, \ldots, x_c) = (y_1, \ldots, y_c)$ is the morphism defined by;

$y_c = x_c$

$y_i = x_i + \frac{\nu_i}{\nu_c} x_c$, $(1 \leq i \leq c-1)$

determined by the conditions (B). Moreover, we can assume that $pr_{c-1}(W) \cap \mathcal{R}^{c-1} \neq \emptyset$. Moving the tuple $(d_1, \ldots d_{c-1})$ along $pr_{c-1}(W)$, we can fine $d_{i_0} > 0$, and d_j, $1 \leq j \leq c-1$, $j \neq i_0$, with $d_j > 0$, so that $\frac{-\nu_c d_{i_0}}{\nu_{i_0}} \neq \frac{-\nu_c \sigma}{w}$ and v_{i_0} is the highest root of $r(x)$, so that the roots w_i of $w(x)$ do not coincide with the highest root v_{i_0} of $r(x)$.

Replacing y with $\epsilon(t) - \epsilon(0)$, and letting $\delta(t) = \gamma(\epsilon(t) - \epsilon(0))$, we have that;

$$\theta(\delta(t), \epsilon(t) - \epsilon(0)) = q(\delta(t)) - (\epsilon(t) - \epsilon(0)) - \epsilon(0) = q(\delta(t)) - \epsilon(t) = 0$$

Then $\delta(t) > 0$, and we can set $n_c = \frac{1}{\delta(t)}$, with $n_c(0) = \frac{1}{v_0}$ Using the linkage relations, we can define $n_i(t)$, for $1 \leq i \leq c-1$ from n_c. As, by (D), we have that $n_i(0) > 0$, for $1 \leq i \leq c$, by continuity, for sufficiently small t, we have that $n_i(t) > 0$, for $1 \leq i \leq c$ as well.

If $w < 0$, we can take the reciprocal of the relation $(\dagger)$, replace ν_i by $-\nu_i$ and $\epsilon(t)$ by $\frac{1}{\epsilon(t)} > 0$, to get $w > 0$. Reordering so that the pivot $\nu_c < 0$, $\nu_i > 0$, for $1 \leq i \leq p'$, $\nu_i < 0$, for $p' + 1 \leq i \leq c - 1$, we can carry out the above proof to get the result.

If $w = 0$, we can carry out the first calculation with β replaced by $\prod_{i=p+1}^{c-1} (\frac{\nu_i}{\nu_c})^{-\nu_i} \neq 0$.

□

Lemma 2.20. *A feasible path γ is a dynamic equilibrium path iff $pr(\gamma_{12}) \subset C_f$, for some $f \in \mathcal{R}_{>0}$, iff $\frac{dQ}{dt} = 0$. In particular, for any feasible path γ in which $pr_{12}(\gamma)$ is fixed, we have dynamic equilibrium and $\frac{dQ}{dt} = 0$.*

Proof. For the first claim, we have that $f > 0$ and if $pr(\gamma_{12}) \subset C_f$, we have that;

$$\prod_{i=1}^{c} x_i^{\nu_i} = f$$

with the same linkage relations as Lemma 2.17. Now follow through Lemma 2.17, noting that differentiating reduces the constant f to 0, as in the proof. Conversely, if $pr(\gamma_{12}) \not\subset C_f$, then we have that;

$$(\prod_{i=1}^{c} x_i^{\nu_i})'|_0 = Q(\gamma(t))'|_0$$

$$= (grad(Q)|_{\gamma(0)} \cdot \gamma'(0)) \neq 0$$

but, if γ is a dynamic equilibrium path, then clearly each n_i is constant, $1 \leq i \leq c$, n is constant and x_i is constant, so that $x_i' = 0$, for $1 \leq i \leq c$ and $(\prod_{i=1}^{c} x_i^{\nu_i})'|_0 = 0$, which is a contradiction. For the second claim, if $pr(\gamma_{12}) \subset C_c$, for some $c \in \mathcal{R}$, it follows from

Definition 2.18 and the proof of Lemma 2.17, that Q is constant and $\frac{dQ}{dt} = 0$. Conversely, if $\frac{dQ}{dt} = 0$, then Q is constant along $pr(\gamma_{12})$, so that $pr(\gamma_{12}) \subset C_c$, for some $c \in \mathcal{R}$. The final claim follows from the fact that Q depends only on the coordinates (T, P), so that $\frac{dQ}{dt} = 0$, and the first claim.

□

Lemma 2.21. *We have that the condition of chemical equilibrium defines a* 1*-dimensional curve* D *in the state space* (T, P)*. Similarly, the conditions that* $Q(T, P) = c$ *define* 1*-dimensional curves* C_c *in* (T, P)*, and if* $\gamma : [0, 1] \to (T, P, n_1, \dots n_c)$ *is a path, such that* $pr_{12}(\gamma)$ *lies in* C_c*, then it must be a dynamic equilibrium path. Let* D' *be a component of* D*, then* Q *is constant along* D' *iff* $\frac{\Delta G^\circ}{T}$ *is constant along* D'*. Let* C'_c *be a component of* C_c*, then* $(\frac{\partial G}{\partial \xi})|_{T,P} = 0$ *along* C'_c *iff* $\frac{\Delta G^\circ}{T} = -Rln(c)$*. Assuming that* $\frac{\Delta G^\circ}{T}$ *is non constant, we have that* Q *is constant along* D' *iff* $pr_1(D')$ *is a fixed temperature* T*, and* $(\frac{\partial G}{\partial \xi})|_{T,P} = 0$ *along* C'_c *iff* $pr_1(C'_c)$ *is a fixed temperature* T*. The only feasible paths which are both chemical and dynamic equilibrium paths are straight line chemical equilibrium paths. There exists a feasible dynamic equilibrium path, with* $pr_{12}(\gamma) \subset P = P^\circ$*.*

Proof. For the first part, either use the fact that $(\frac{\partial G}{\partial \xi})|_{T,P}$ only depends on (T, P) and differentiability properties, or the result from Lemma 2.10 that chemical equilibrium is defined by $Q(T, P) - e^{\frac{-\Delta G^\circ}{RT}} = 0$, and the fact that ΔG° depends on T. For the second part, either use differentiability properties of $Q(T, P)$ or the fact from Lemma 2.10 that $Q = 1$ iff $(\frac{\partial G}{\partial \xi})|_{T,P} - \Delta G^\circ = 0$. The second claim is clear from Lemma 2.20. For the third claim, we have, by Lemma 2.10, that along D', $Q = e^{\frac{\Delta G^\circ}{RT}}$, so that clearly Q is constant along D' iff $\frac{\Delta G^\circ}{T}$ is constant. The fourth claim is clear by the fact that $(\frac{\partial G}{\partial \xi})|_{T,P} - \Delta G^\circ = RTln(c)$ along C'_c. The fifth and sixth claims follow immediately from the fact that $\frac{\Delta G^\circ}{T}$ is a function of T and is non constant. For the seventh claim, if γ is a chemical and dynamic equilibrium path, then $pr_{12}(\gamma) \subset D$, and, by Lemma 2.20, $pr_{12}(\gamma) \subset C_c$, for some $c \in \mathcal{R}$. It follows that Q is constant along the $pr_{12}(\gamma) \subset D'$ for some component D', and then, by the fifth claim, $pr_1(\gamma) \subset pr_1(D')$ is a fixed temperature T, so that γ is a straight line chemical equilibrium path. For the final claim, we have that $Q(T, P^\circ) = 1$, by Lemma 2.17, so that $P = P^\circ$ lies in C_1. It follows, by Lemma 2.20, that a feasible path γ with $pr_{12}(\gamma) \subset P = P^\circ$ is a dynamic equilibrium path. □

3. Ideal Solutions

Remarks 3.1. *We have, using the phase rule for an ideal solution in equilibrium with its vapour, and using the ideal gas law, see* [10]*, that;*

$$\mu_i^{(g)} = \mu_i^{\circ(g)} + RTln(\tfrac{P_i}{P^\circ})$$

$$\mu_i^{(sol)} = \mu_i^{\circ(sol)} + RTln(\tfrac{P_i}{P^\circ})\ (*)$$

By the definition of an ideal solution, we have that;

$$\mu_i = \mu_i^* + RTln(x_i)\ (**)$$

where, by $\mu_i^*(T,P)$*, we mean the chemical potential of substance* i *on its own, at temperature and pressure* (T,P)*. By Raoult's law* $P_i = x_i P_i^*$*, see* [9]*, combined with* $(**)$*, we obtain;*

$$\mu_i = \mu_i^* + RTln(x_i)$$

$$= \mu_i^* + RTln(\tfrac{P_i}{P_i^*})$$

$$= \mu_i^* + RTln(\tfrac{P_i}{P^\circ}) - RTln(\tfrac{P_i^*}{P^\circ})\ (***)$$

Combining $(*), (***)$*, we obtain that;*

$$\mu_i^* = \mu_i - RTln(\tfrac{P_i}{P^\circ}) + RTln(\tfrac{P_i^*}{P^\circ})$$

$$= (\mu_i^\circ + RTln(\tfrac{P_i}{P^\circ})) - RTln(\tfrac{P_i}{P^\circ}) + RTln(\tfrac{P_i^*}{P^\circ})$$

$$= \mu_i^\circ + RTln(\tfrac{P_i^*}{P^\circ})\ (\dagger)$$

Letting $P_i^* = P^\circ$, (4), *we obtain that* $\mu_i^*(T, P') = \mu_i^\circ$, $(****)$, *where* (T, P') *is the temperature and pressure at which the equilibrium pressure* $P_i'^* = P^\circ$. *From* $(**)$, *the fact that* $\mu_i^*(T, P) \simeq \mu_i^*(T, P')$ *and*

4

We need a version of the Clapeyron equation, in which the temperature of substance i in the liquid (I) and gas phases (II) is fixed and equal, but the liquid pressure is changed. We have that, from the definition of Gibbs energy, the product rule for differentials that, the definition of entropy $dS = \frac{dQ}{T}$ and the first law of thermodynamics $dQ = dU + PdV$;

$$dG = dU + PdV + VdP - TdS - SdT$$

$$= dU + PdV + VdP - dQ - SdT$$

$$= -SdT + VdP$$

so that, as the two phases are in equilibrium, dividing by the number of moles;

$$dG_m^{(I)} = -S_m^{(I)}dT + V_m^{(I)}dP$$

$$= dG_m^{(II)}$$

$$= -S_m^{(II)}dT + V_m^{(II)}dP''$$

As the temperature is fixed, $dT = 0$, so that;

$$V_m^{(I)}dP = V_m^{(II)}dP''$$

$$\frac{dP''}{dP} = \frac{V_m^I}{V_m^{II}}$$

By the ideal gas law $V_m^{II} = \frac{RT}{P''}$, so that;

$$\frac{dP''}{dP} = \frac{V_m^I P''}{RT}$$

Assuming $V_m^{(I)}(T, P)$ is approximately constant, in particularly bounded and positive, we obtain that, integrating;

$$ln(P'') = \frac{V_m^I P}{RT}$$

$$P''(P) = A(T)e^{\frac{V_m^I P}{RT}}$$

As, for fixed T, there exists a unique $P_0(T)$, described by the Clausius-Clapeyron equation, for which $P''(P_0(T)) = P_0(T)$, we have, in particular, that;

$$P_0(T) = A(T)e^{\frac{V_m^I P_0(T)}{RT}}$$

so that;

$(****)$, *we obtain that;*

$$\mu_i \simeq \mu_i^\circ + RTln(x_i), \ (*****)$$

as a very good approximation. This avoids the contradiction that $x_i = 1$ *for a solution involving more than one component, at* $P = P^\circ$. *To make the results here more precise, we need to compute the error term, but the proof is still consistent if we allow that* $n_i(T, P) \to 0$ *as* $P \to P^\circ$, *so that* $x_i = \frac{n_i}{n} \to 1$, *and* x_i *is not defined at* $P = P^\circ$.

More specifically, we have that;

$$\mu_i^*(T, P) = \mu_i^*(T, P') + \delta$$

where $\delta = \mu_i^*(T, P) - \mu_i^*(T, P')$, *so that;*

$$\mu_i = \mu_i^\circ + RTln(x_i) + \delta$$

For Raoult's law, see [9], *we also need an approximation. We have that, by the definition of an ideal solution, the phase rule, Dalton's law that each gas in a mixture of ideal gases behaves as if it were alone in the container at the equilibrium pressures* $\{P_i, P_i^*\}$, *see* [9], *that;*

$$\mu_i = \mu_i^* + RTln(x_i)$$

$$= \mu_i^*(T, P_i^*) + RTln(x_i) + \epsilon$$

$$= \mu_i^{\circ(g)} + RTln(\tfrac{P_i^*}{P^\circ}) + RTln(x_i) + \epsilon$$

$$= \mu_i^{\circ(g)} + RTln(\tfrac{P_i}{P^\circ})$$

so that;

$A(T) = P_0(T)e^{-\frac{V_m^I P_0(T)}{RT}}$

$P''(P) = P_0(T)e^{\frac{V_m^I (P - P_0(T))}{RT}}$

Note that as $\frac{V_m^I P_0(T)}{RT} << 1$, the theoretical second value $P_1(T)$, for which $P''(P_1(T)) = P_1(T)$ lies outside the normal range of pressures. Moreover, as $P^\circ > P_0(T)$, for fixed T, in a reasonable range close to room temperature, there exists P', with $P''(P', T) = P^\circ$

$RTln(x_i) = RTln(\frac{P_i}{P^\circ}) - RTln(\frac{P_i^*}{P^\circ}) - \epsilon$

where $\epsilon = \mu_i^*(T,P) - \mu_i^*(T,P_i^*)$*, so that* $(***)$ *becomes;*

$\mu_i = \mu_i^* + RTln(x_i)$

$= \mu_i^* + RTln(\frac{P_i}{P^\circ}) - RTln(\frac{P_i^*}{P^\circ}) - \epsilon \ (***)'$

Combining $(*), (***)'$*, we obtain that;*

$\mu_i^* = \mu_i - RTln(\frac{P_i}{P^\circ}) + RTln(\frac{P_i^*}{P^\circ}) + \epsilon$

$= (\mu_i^\circ + RTln(\frac{P_i}{P^\circ})) - RTln(\frac{P_i}{P^\circ}) + RTln(\frac{P_i^*}{P^\circ}) + \epsilon$

$= \mu_i^\circ + RTln(\frac{P_i^*}{P^\circ}) + \epsilon \ (\dagger)'$

Letting $P_i^* = P^\circ$ *again, we obtain that* $\mu_i^*(T,P') = \mu_i^\circ + \epsilon$*,* $(****)'$

From $(**)$*,* $(****)'$*, we obtain that;*

$\mu_i = \mu_i^* + RTln(x_i)$

$= \mu_i^*(T,P') + \delta + RTln(x_i)$

$= \mu_i^\circ + \epsilon + \delta + RTln(x_i)$

$= \mu_i^\circ + RTln(x_i) + \gamma_i$

where $\gamma_i = \epsilon + \delta = \mu_i^*(T,P) - \mu_i^*(T,P_i^*) + \mu_i^*(T,P) - \mu_i^*(T,P')$

$= 2\mu_i^*(T,P) - \mu_i^*(T,P_i^*) - \mu_i^*(T,P') \simeq 0$

Using Lemma 2.5, we have that $dG = -SdT + VdP$*, so that, if temperature is fixed,* $dG = VdP$*, then, for the Gibbs energy function of substance* i *on it own, in the liquid phase;*

$\mu_i^*(T,P) - \mu_i^*(T,P_i^*) = \frac{G(T,P,n) - G(T,P_i^*,n)}{n}$

$= \frac{1}{n}\int_{P_i^*}^{P} dG$

$= \frac{1}{n}\int_{P_i^*}^{P} V dP$

$= \frac{1}{n}\int_{P_i^*}^{P} \frac{nN_A m_i}{\kappa_i(T,P)} dP$

$\simeq \frac{N_A m_i (P - P_i^*)}{\kappa}$

$= V_{m,i}(P - P_i^*)$

where $\kappa(T,P)$ is the density of substance i in the liquid phase, and which we assume to be approximately constant, and $V_{m.i}$ is the molar volume. Similarly;

$\mu_i^*(T,P) - \mu_i^*(T,P') \simeq \frac{N_A m_i (P - P')}{\kappa}$

$= V_{m,i}(P - P')$

so that;

$\gamma_i(T,P) \simeq V_{m,i}(2P - P_i^* - P') \simeq 0$

We reformulate Lemmas 2.8, 2.10, 2.11 and 2.12 with this error term;

Lemma 3.2. *In the ideal solution case, for the energy function G involving only c uncharged species;*

$(\frac{\partial G}{\partial \xi})_{T,P} = \Delta G^\circ + RTln(Q) + \epsilon$

where $\epsilon(T,P) = \sum_{i=1}^{c} \nu_i \gamma_i(T,P) \simeq 0$ and $\gamma_i(T,P) \simeq 0$ is the error term for the i'th uncharged species in Remark 3.1.

Proof. By Lemma 2.10, we have that;

$(\frac{\partial G}{\partial \xi})_{T,P} = \sum_{i=1}^{c} \nu_i \mu_i$

$\Delta G^\circ = \sum_{i=1}^{c} \nu_i \mu_i^\circ$, $(*)$

Using $(*)$, the fact that $\mu_i = \mu_i^\circ + RTln(a_i) + \gamma_i$, and Definition 2.1, we have that;

$(\frac{\partial G}{\partial \xi})_{T,P} - \Delta G^\circ = \sum_{i=1}^{c} \nu_i (\mu_i - \mu_i^\circ)$

$= \sum_{i=1}^{c} \nu_i(\mu_i^\circ + RTln(a_i) + \gamma_i - \mu_i^\circ)$

$= \sum_{i=1}^{c} \nu_i RTln(a_i) + \sum_{i=1}^{c} \nu_i\gamma_i$

$= RTln(\prod_{i=1}^{c} a_i^{\nu_i}) + \sum_{i=1}^{c} \nu_i\gamma_i = RTln(Q) + \epsilon$

□

Lemma 3.3. *For an ideal solution, we have, using the definition of $\epsilon(P)$ in Lemma 3.2, and the error terms $\gamma_i(T,P)$, $1 \leq i \leq c$ in Remark 3.1, that;*

$(\frac{\partial G}{\partial \xi})_{T,P} = \sum_{i=1}^{c} \nu_i\mu_i$

$\Delta G^\circ = \sum_{i=1}^{c} \nu_i\mu_i^\circ$

At chemical equilibrium T, P, $(\frac{\partial G}{\partial \xi})_{T,P} = 0$ and at T, P^0, $\Delta G^\circ = 0$.

If chemical and electrical chemical equilibrium exists at (T, P°) and (T, P), $Q(T,P) = e^{\frac{-\epsilon(T,P)}{RT}} \simeq 1$ and $E = E^\circ$. Conversely, if $Q(T,P) = e^{\frac{-\epsilon(T,P)}{RT}} \simeq 1$ and chemical equilibrium exists at (T, P°) then chemical equilibrium exists at (T, P).

Chemical equilibrium exists at (T, P) iff $Q(T,P) = e^{\frac{-\Delta G^\circ - \epsilon(T,P)}{RT}}$

We always have that $Q(T, P^\circ) = e^{\frac{-\delta}{RT}} \simeq 1$, where;

$\delta(T) = \epsilon(T, P^\circ) = \sum_{i=1}^{c} \nu_i\gamma_i(T, P^\circ)$

Proof. For the first claim, we have, using the definition of ξ, that;

$dn_i = \nu_i d\xi$, $(1 \leq i \leq c)$, $(*)$

By Lemma 2.5, fixing T and P, and using $(*)$, we have that;

$dG = \sum_{i=1}^{c} \mu_i dn_i$

$= (\sum_{i=1}^{c} \mu_i\nu_i)d\xi$, $(\dagger)$

so that;

$(\frac{\partial G}{\partial \xi})_{T,P} = \sum_{i=1}^{c} \mu_i \nu_i$, (††)

The second claim from the first, as;

$\Delta G^\circ(T) = \int_0^1 (\frac{\partial G}{\partial \xi})_{T,P^\circ}$

$= \int_0^1 (\sum_{i=1}^{c} \nu_i \mu_i^\circ(T)) d\xi$

$= \sum_{i=1}^{c} \nu_i \mu_i^\circ(T) \int_0^1 d\xi$

$= \sum_{i=1}^{c} \nu_i \mu_i^\circ(T)$

noting that $(\frac{\partial G}{\partial \xi})_{T,P^\circ}$ doesn't vary with ξ. For the third claim, at chemical equilibrium, T, P, noting again that $(\frac{\partial G}{\partial \xi})_{T,P}$ doesn't vary with ξ, and using (†, ††), we have that;

$dG = (\frac{\partial G}{\partial \xi})_{T,P} = 0$, (independently of ξ) (†††)

At chemical equilibrium T, P°, using the first and second claims, and (†††), we have that;

$dG = (\frac{\partial G}{\partial \xi})_{T,P^\circ}$

$= \sum_{i=1}^{c} \nu_i \mu_i^\circ$

$= \Delta G^\circ = 0$

For the second to last claim, and the first direction, we have, by Lemma 3.2, that $RTln(Q) = -\epsilon(T,P) \simeq 0$, so that $Q(T,P) = e^{\frac{-\epsilon(T,P)}{RT}} \simeq 1$, and, by Lemma 4.1, that $E - E^\circ = -\frac{RTln(Q)}{2F} - \frac{\epsilon(T,P)}{2F} = \frac{\epsilon(T,P)}{2F} - \frac{\epsilon(T,P)}{2F} = 0$. For the converse, we have by Lemma 2.8, using the fact that $Q(T,P) = e^{\frac{-\epsilon(P)}{RT}} \simeq 1$;

$(\frac{\partial G}{\partial \xi})_{T,P} = \Delta G^\circ - \epsilon(T,P) + \epsilon(T,P) = \Delta G^\circ$

and, if chemical equilibrium exists at (T, P°), then, as $Q(T,P^\circ) = e^{\frac{-\epsilon(T,P^\circ)}{RT}}$ we have that;

$(\frac{\partial G}{\partial \xi})_{T,P^\circ} = \Delta G^\circ + RTln(Q(T,P^\circ) + \epsilon(T,P^\circ) = \Delta G^\circ = 0$

so that $(\frac{\partial G}{\partial \xi})_{T,P} = 0$

For the penultimate claim, in one direction, use Lemma 2.8, together with the fact that $(\frac{\partial G}{\partial \xi})_{T,P} = 0$ and rearrange, the converse is also clear, applying ln.

For the final claim, we have, by the definition of activities, that;

$\mu_i = \mu_i^\circ + RTln(a_i) + \gamma_i(T, P)$

so that $RTln(a_i(T, P^\circ)) = -\gamma_i(T, P^\circ)$. Now use the definition of Q in Definition 2.1.

□

Lemma 3.4. *Along a chemical equilibrium path, we have that;*

$ln(\frac{Q(T_2)}{Q(T_1)}) = \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^\circ}{T^2} dT + + \frac{1}{R}(\frac{\epsilon(P(T_1))}{T_1} - \frac{\epsilon(P(T_2))}{T_2})$

$\frac{\Delta G^\circ(T_2)}{T_2} - \frac{\Delta G^\circ(T_1)}{T_1} = -\int_{T_1}^{T_2} \frac{\Delta H^\circ}{T^2} dT$

In particularly, if ΔH° is temperature independent;

$ln(\frac{Q(T_2)}{Q(T_1)}) = -\frac{\Delta H^\circ}{R}(\frac{1}{T_2} - \frac{1}{T_1}) + \frac{1}{R}(\frac{\epsilon(P(T_1))}{T_1} - \frac{\epsilon(P(T_2))}{T_2})$

$\frac{\Delta G^\circ(T_2)}{T_2} - \frac{\Delta G^\circ(T_1)}{T_1} = \Delta H^\circ(\frac{1}{T_2} - \frac{1}{T_1})$

$\Delta G^\circ(T_1) = \frac{T_1}{T_2}\Delta G^\circ(T_2) - (\frac{T_1}{T_2} - 1)\Delta H^\circ$

For $c \in \mathcal{R}$, Let D_c intersect the line $P = P^\circ$ at (T_1, P°), then, for $(T_2, P) \in D_c$, we have that;

$Q(T_2, P) = e^{\frac{\Delta G^\circ(T_1) - \Delta G^\circ(T_2) - \epsilon(T_2, P(T_2))}{RT_2}}$ (†††)

$c = \Delta G^\circ(T_1)$

$ln(\frac{Q(T_2)}{Q(T_1)}) = ln(Q(T_2)) = \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^\circ - c}{T^2} dT - (\frac{\epsilon(T_2, P(T_2))}{RT_2} - \frac{\epsilon(T_1, P(T_1))}{RT_1})$

$\frac{\Delta G^\circ(T_2) - \Delta G^\circ(T_1)}{T_2} = -\int_{T_1}^{T_2} \frac{\Delta H^\circ - c}{T^2} dT$

and if ΔH° is temperature independent;

$ln(\frac{Q(T_2)}{Q(T_1)}) = ln(Q(T_2)) = -(\frac{\Delta H^\circ - c}{R})(\frac{1}{T_2} - \frac{1}{T_1}) - (\frac{\epsilon(P(T_2))}{RT_2} - \frac{\epsilon(P(T_1))}{RT_1})$ (††)

$\frac{\Delta G^\circ(T_2) - \Delta G^\circ(T_1)}{T_2} = (\Delta H^\circ - c)(\frac{1}{T_2} - \frac{1}{T_1})$ (†)

$\Delta G^\circ(T_1) = \frac{T_1}{T_2}\Delta G^\circ(T_2) - \Delta H^\circ(\frac{T_1}{T_2} - 1)$ (††††)

Proof. By Lemma 2.10, we have that;

$\Delta G^\circ = \sum_{i=1}^{c} \nu_i \mu_i^\circ$

so that differentiating with respect to T;

$\frac{d(\Delta G^\circ)}{dT} = \sum_{i=1}^{c} \nu_i \frac{d\mu_i^\circ}{dT}$

$= \sum_{i=1}^{c} \nu_i (\frac{\partial \mu_i^\circ}{\partial T})_{P,n}$

By Euler reciprocity, we have that;

$(\frac{\partial \mu_i^\circ}{\partial T})_{P,n} = -(\frac{\partial S^\circ}{\partial n_i})_{T,P,n'} = -\overline{S}_i^\circ$

so that, noting $\overline{S}_i^\circ$ is independent of n_i, so we can replace $\overline{S}_i^\circ$ by $\overline{S}_{m,i}^\circ$, the absolute molar entropy of substance i, and using thermodynamic arguments;

$\frac{d(\Delta G^\circ)}{dT} = -\sum_{i=1}^{c} \nu_i \overline{S}_i^\circ =$

$= -\sum_{i=1}^{c} \nu_i \overline{S}_{m,i}^\circ$

$= -\Delta S^\circ$ $(*)$

Using the product rule, $(*)$ and the definition of enthalpy, we have that;

$\frac{d}{dT}(\frac{\Delta G^\circ}{T}) = \frac{1}{T}\frac{d(\Delta G^\circ)}{dT} - \frac{1}{T^2}\Delta G^\circ$

$= -\frac{\Delta S^\circ}{T} - \frac{\Delta G^\circ}{T^2}$

$= -\frac{\Delta (ST+G)^\circ}{T^2}$

$= -\frac{\Delta H^\circ}{T^2}$ $(**)$

By Lemma 3.3, along a chemical equilibrium path, we have that $Q = e^{\frac{-\Delta G^\circ - \epsilon(T,P)}{RT}}$, so that $ln(Q) = \frac{-\Delta G^\circ - \epsilon(P)}{RT}$. It follows from $(**)$ that;

$\frac{dln(Q)}{dT} = \frac{d}{dT}(\frac{-\Delta G^\circ}{RT}) - \frac{d}{dT}(\frac{\epsilon(P)}{RT})$

$= \frac{\Delta H^\circ}{RT^2} - \frac{d}{dT}(\frac{\epsilon(P)}{RT})$

It follows, integrating between T_1 and T_2, and using the fundamental theorem of calculus, that;

$ln(\frac{Q(T_2)}{Q(T_1)}) = ln(Q)(T_2) - ln(Q)(T_1)$

$= \int_{T_1}^{T_2} \frac{dln(Q)}{dT} dT$

$= \frac{1}{R} \int_{T_1}^{T_2} [\frac{\Delta H^\circ}{T^2} - \frac{d}{dT}(\frac{\epsilon(P)}{RT})] dT$

$= \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta H^\circ}{RT_1} - (\frac{\epsilon(P(T_2))}{RT_2} - \frac{\epsilon(P(T_1))}{RT_1})$ (P)

so that, rearranging, we obtain the first claim. Using the fact, by Lemma 3.2, that;

$ln(Q(T_2)) = \frac{-\Delta G^\circ(T_2) - \epsilon(P(T_2,T_2))}{RT_2}$

$ln(Q(T_1)) = \frac{-\Delta G^\circ(T_1) - \epsilon(T_1,P(T_1))}{RT_1}$

we obtain, substituting into (P), canceling R, and performing the integration, if ΔH° is temperature independent, that;

$\frac{-\Delta G^\circ(T_2) - \epsilon(T_2,P(T_2))}{RT_2} - \frac{-\Delta G^\circ(T_1) - \epsilon(T_1,P(T_1))}{RT_1} = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta H^\circ}{RT_1} - (\frac{\epsilon(T_2,P(T_2))}{RT_2} - \frac{\epsilon(T_1,P(T_1))}{RT_1})$

so that;

$\frac{\Delta G^\circ(T_2)}{T_2} - \frac{\Delta G^\circ(T_1)}{T_1} = \Delta H^\circ(\frac{1}{T_2} - \frac{1}{T_1})$ (Q)

For the fifth claim, rearrange (Q). If D_c intersects the line $P = P^\circ$ at (T_1, P°), for the sixth $(\dagger\dagger\dagger)$ and seventh claims, we have, using Lemma 3.2 and the fact from Lemma 3.3 that $Q(T_1, P^\circ) = e^{\frac{-\delta(T_1)}{RT_1}}$;

$(\frac{\partial G}{\partial \xi})_{T_2,P} = \Delta G^\circ(T_2) + RT_2 ln(Q(T_2, P)) + \epsilon(T_2, P(T_2))$

$= (\frac{\partial G}{\partial \xi})_{T_1,P^\circ}$

$= \Delta G^\circ(T_1) + RT_1 ln(Q(T_1,P^\circ)) + \epsilon(T_1,P(T_1))$

$= \Delta G^\circ(T_1) + RT_1 ln(Q(T_1,P^\circ)) + \epsilon(T_1,P^\circ)$

$= \Delta G^\circ(T_1) - \delta(T_1) + \epsilon(T_1,P^\circ)$

$= \Delta G^\circ(T_1) = c$

so that, again rearranging, we obtain the result. Along D_c, we have, using Lemma 3.2, that;

$ln(Q(T)) = \frac{c-\Delta G^\circ(T)-\epsilon(T,P(T))}{RT}$

so that, using the first part;

$\frac{dln(Q)}{dT} = \frac{d}{dT}(\frac{c-\Delta G^\circ(T)-\epsilon(T,P(T))}{RT})$

$= \frac{-c}{RT^2} + \frac{d}{dT}(\frac{-\Delta G^\circ(T)}{RT}) - \frac{d}{dT}(\frac{\epsilon(T,P(T))}{RT})$

$= \frac{\Delta H^\circ - c}{RT^2} - \frac{d}{dT}(\frac{\epsilon(T,P(T))}{RT})$

so that, performing the integration, using the fact that $Q(T_1,P^\circ) = e^{\frac{-\delta(T_1)}{RT_1}}$;

$ln(Q(T_2)) - ln(Q(T_1)) = ln(Q(T_2)) + \frac{\delta(T_1)}{RT_1} = \frac{1}{R}\int_{T_1}^{T_2}[\frac{\Delta H^\circ - c}{T^2} - \frac{d}{dT}(\frac{\epsilon(T,P(T))}{RT})]dT$

$= \frac{1}{R}\int_{T_1}^{T_2}\frac{\Delta H^\circ - c}{T^2}dT - (\frac{\epsilon(T_2,P(T_2))}{RT_2} - \frac{\epsilon(T_1,P(T_1))}{RT_1})$

We have that, by Lemmas 3.2 and 3.3;

$ln(Q(T_2)) = \frac{c-\Delta G^\circ(T_2)-\epsilon(T_2,P(T_2))}{RT_2}$

$ln(Q(T_1)) = -\frac{\delta(T_1)}{RT_1}$

so that;

$ln(Q(T_2)) - ln(Q(T_1)) = \frac{c-\Delta G^\circ(T_2)-\epsilon(T_2,P(T_2))}{RT_2} + \frac{\delta(T_1)}{RT_1}$

$= \frac{\Delta G^\circ(T_1) - \Delta G^\circ(T_2) - \epsilon(T_2, P(T_2))}{RT_2} + \frac{\delta(T_1)}{RT_1}$

$= \frac{1}{R}\int_{T_1}^{T_2}[\frac{\Delta H^\circ - c}{T^2}]dT - (\frac{\epsilon(T_2,P(T_2))}{RT_2} - \frac{\epsilon(T_1,P(T_1))}{RT_1})$

$= \frac{-1}{R}(\Delta H^\circ - c)(\frac{1}{T_2} - \frac{1}{T_1}) - (\frac{\epsilon(T_2,P(T_2))}{RT_2} - \frac{\delta(T_1)}{RT_1})$

so that, cancelling R and the the error terms;

$\frac{\Delta G^\circ(T_2) - \Delta G^\circ(T_1)}{T_2} = (\Delta H^\circ - c)(\frac{1}{T_2} - \frac{1}{T_1})$

$= (\Delta H^\circ - \Delta G^\circ(T_1))(\frac{1}{T_2} - \frac{1}{T_1})$

so that, rearranging again;

$\Delta G^\circ(T_1)(\frac{1}{T_1} + \frac{1}{T_2} - \frac{1}{T_2}) = \frac{\Delta G^\circ(T_1)}{T_1}$

$= \frac{\Delta G^\circ(T_2)}{T_2} - \Delta H^\circ(\frac{1}{T_2} - \frac{1}{T_1})$

to obtain;

$\Delta G^\circ(T_1) = \frac{T_1}{T_2}\Delta G^\circ(T_2) - \Delta H^\circ(\frac{T_1}{T_2} - 1)$

□

Lemma 3.5. *If there exists a component D_c, $c \in \mathcal{R}$, which projects onto a closed bounded subinterval I of the line $P = P^\circ$, not containing 0, and intersects $P = P^\circ$ at (T_1, P°), with $T_1 > 0$, then, for $T_2 \in I$, ΔG° is linear, with;*

$\Delta G^\circ(T_2) = T_2(\frac{(\Delta G^\circ(T_1) - \Delta H^\circ)}{T_1}) + \Delta H^\circ$

for $T_2 \in I$. If $\epsilon \neq 0$, have that;

$(\frac{dG}{d\xi})_{T,P} = \lambda + \epsilon P + \beta T$

where $\{\lambda, \epsilon, \beta\} \subset \mathcal{R}$ and $\{\beta, \epsilon\}$ can be effectively determined, and we have that the activity coefficient is given by;

$Q(T_1, P') = e^{\frac{\epsilon(P' - P'^\circ) - \epsilon(T_1, P')}{RT_1}}$

and the dynamic equilibrium paths are given by;

$P' = P'^{\circ} + \frac{RT_1 ln(c) + \epsilon(P', T_1)}{\epsilon}$

for $c \in \mathcal{R}_{\geq 0}$*, see Definition 2.1, while the quasi-chemical equilibrium paths are given by;*

$\lambda + \epsilon P' + \beta T_1 = c$

for $c \in \mathcal{R}$*.*

If $\epsilon = 0$*;*

$(\frac{dG}{d\xi})_{T,P} = \lambda + \beta T + \sigma ln(T)$

where $\{\lambda, \beta, \sigma\} \subset \mathcal{R}$*, and* $\{\beta, \sigma\}$ *can be effectively determined. The activity coefficient* Q *is given by;*

$Q(T_1, P') = e^{\frac{-\epsilon(T_1, P')}{RT_1}}$

The dynamic equilibrium paths are given by;

$e^{\frac{-\epsilon(T_1, P')}{RT_1}} = c$

for $c \in \mathcal{R}_{\geq 0}$*, see Definition 2.1, while the quasi-chemical equilibrium paths are given by;*

$\lambda + \epsilon P' + \beta T_1 = c$

for $c \in \mathcal{R}$*.*

Proof. For the first claim, by Lemma 3.4, we have that;

$\Delta G^{\circ}(T_2) = \frac{T_2}{T_1}\Delta G^{\circ}(T_1) - \Delta H^{\circ}(\frac{T_2}{T_1} - 1)$

$= T_2(\frac{(\Delta G^{\circ}(T_1) - \Delta H^{\circ})}{T_1}) + \Delta H^{\circ}$

For the next claim, following the proof of Lemma 2.12 again, we have that;

$\frac{dG}{d\xi}_{T,P} = \lambda + \epsilon P + \beta T + \sigma ln(T)$ (D)

where $\{\beta, \epsilon, \lambda, \sigma\} \subset \mathcal{R}$.

If $\epsilon = 0$, then $(\frac{dG}{d\xi})_{T,P}$ is independent of P, and the components D_c are all straight line paths. In this case, if D_c intersects the line $P = P^\circ$ at (T_1, P°), then, for all $P > 0$;

$$c = \Delta G^\circ(T_1) + RT_1 ln(Q(T_1, P) + \epsilon(P)$$

$$= \Delta G^\circ(T_1)$$

implies that $RT_1 ln(Q(T_1, P) = -\epsilon(T_1, P)$, so that $Q(T_1, P) = e^{\frac{-\epsilon(T_1,P)}{RT_1}}$, (X). From (D), we have that;

$$(\tfrac{dG}{d\xi})_{T,P} = \lambda + \beta T + \sigma ln(T), \ (Y)$$

The calculation of the dynamical and chemical equilibrium paths follows easily, from the equations $Q = c$, for $c \in \mathcal{R}_{\geq 0}$ and $(\frac{dG}{d\xi})_{T,P} = c$, for $c \in \mathcal{R}$, using $(X), (Y)$.

If $\epsilon \neq 0$, there exists a component D_c given by;

$$\lambda + \epsilon P + \beta T + \sigma ln(T) = c$$

projecting generically onto the line $P = P^0$. Calculating limits at $\{+\infty, -\infty\}$, we have that for $\beta > 0, \sigma > 0$ or $\beta < 0, \sigma < 0$, we can solve the equation;

$$\lambda + \epsilon P^\circ + \beta T + \sigma ln(T) = c \ (Z)$$

for T. If $\beta > 0, \sigma < 0$ or $\beta < 0, \sigma > 0$, observing that $(\beta T + \sigma ln(T))' = \beta + \frac{\sigma}{T}$, $(\beta T + \sigma ln(T))'' = -\frac{\sigma}{T^2}$, so there exists a min/max at $T = \frac{-\sigma}{\beta}$, we have that, if;

$$-\sigma + \sigma ln(\tfrac{-\sigma}{\beta}) \leq c - \lambda - \epsilon P^\circ$$

$$-\sigma + \sigma ln(\tfrac{-\sigma}{\beta}) \geq c - \lambda - \epsilon P^\circ$$

we can again solve the equation (Z) for T, so that, for an appropriate choice of c, there exists an intersection of the component D_c with the line $P = P^\circ$.

By the first part, ΔG° is linear, with;

$\Delta G^\circ(T_2) = T_2(\frac{(\Delta G^\circ(T_1) - \Delta H^\circ)}{T_1}) + \Delta H^\circ$

for an intersection at (T_1, P°). We also have, using (D), that;

$\Delta G^\circ(T_2) = (\frac{\partial G}{\partial \xi})_{T,P}(T_2, P^\circ)$

$= \lambda + \epsilon P^\circ + \beta T_2 + \sigma ln(T_2)$

so that, equating coefficients;

$\sigma = 0$

$\lambda + \epsilon ln(P^\circ) = \Delta H^\circ$

$\beta = \frac{(\Delta G^\circ(T_1) - \Delta H^\circ)}{T_1}$

$\Delta G^\circ(T_1) = \beta T_1 + \Delta H^\circ$

We can then, using Lemma 3.2, obtain a formula for the activity coefficient;

$Q(T_1, P') = e^{\frac{((\frac{\partial G}{\partial \xi})_{T,P|_{T_1,P'}} - \Delta G^\circ(T_1)) - \epsilon(T_1,P')}{RT_1}}$

$= e^{\frac{(\Delta H^\circ - \epsilon P'^\circ + \epsilon P' + \beta T_1 - (\beta T_1 + \Delta H^\circ)) - \epsilon(T_1,P')}{RT_1}}$

$= e^{\frac{\epsilon(P' - P'^\circ) - \epsilon(T_1,P')}{RT_1}}$ (W)

as required. The claim about the coefficients being determined is clear from the proof. The determination of the dynamical and quasi-chemical equilibrium lines, see Definitions 2.1 and Lemma 2.20, follows from a simple rearrangement of the formulas $Q(T_1, P') = c$, for some $c \in \mathcal{R}_{\geq 0}$, using (W), and $(\frac{dG}{d\xi})_{T,P} = c$, for some $c \in \mathcal{R}$, using (D), with $\sigma = 0$. □

Lemma 3.6. *Let notation be as in Lemma 2.12, then if* $\epsilon \neq 0$, *with* $Q(T, P) = e^{\frac{\epsilon(P - P^\circ) - \epsilon(P,T)}{RT}}$, *then, using the definition of grad in* [2]*;*

$grad(Q)(T, P) = [\frac{-(\epsilon(P - P^\circ) - \epsilon(T,P)) - T\epsilon_T(T,P)}{RT^2}, \frac{\epsilon - \epsilon_P(T,P)}{RT}]e^{\frac{\epsilon(P - P^\circ) - \epsilon(T,P)}{RT}}$

In particular, for reactions with $\sum_{i=1}^{c} \nu_i^2 - \alpha^2 > 0$, *and* Q *determined as above, where* $\alpha = \sum_{i=1}^{c} \nu_i$, *the paths of maximal reaction (steepest slope) are given by;*

$\frac{dP}{dT} = \frac{T(\epsilon - \epsilon_P(T,P))}{\epsilon(T,P) - \epsilon(P-P^\circ) - T\epsilon_T(T,P)}$

If $\epsilon(T,P) = 0$*;*

$grad(Q)(T,P) = [\frac{-\epsilon(P-P^\circ)}{RT^2}, \frac{\epsilon}{RT}]e^{\frac{\epsilon(P-P^\circ)}{RT}}$

and the paths of maximal reaction are given by;

$(P - P^\circ)^2 = -T^2 + c$

for $c \in \mathcal{R}$. *If* $\epsilon = 0$, *with with* $Q(T,P) = e^{\frac{-\epsilon(T,P)}{RT}}$, *then;*

$grad(Q)(T,P) = (\frac{\epsilon(T,P) - T\epsilon_T(T,P)}{RT^2} e^{\frac{-\epsilon(T,P)}{RT}}, -\frac{\epsilon_P(T,P)}{RT} e^{\frac{-\epsilon(T,P)}{RT}})$

and the paths of maximal reaction are given by;

$\frac{dP}{dT} = -\frac{T\epsilon_P(T,P)}{\epsilon(T,P) - T\epsilon_T(T,P)}$

Proof. The determination of $grad(Q)(T,P) = (\frac{\partial Q}{\partial T}, \frac{\partial Q}{\partial P})$ is a simple application of the chain rule and the formula for Q. By the definition of the extent ξ of a reaction, see Definition 2.1, we have that, for $1 \leq i \leq c$;

$n_i(t) = \nu_i \xi(t) + n_{i,0}$

$n(t) = \sum_{j=1}^{c} n_i(t)$

$= \sum_{i=1}^{c} (\nu_i \xi(t) + n_{i,0})$

$= \alpha \xi(t) + \beta$

where $\alpha = \sum_{i=1}^{c} \nu_i$ and $\beta = \sum_{i=1}^{c} n_{i,0}$

so that;

$x_i(t) = \frac{n_i(t)}{n(t)} = \frac{\nu_i \xi(t) + n_{i,0}}{\alpha \xi(t) + \beta}$

It follows that for a feasible path γ;

$\prod_{i=1}^{c} x_i^{\nu_i}(t) = Q(\gamma_{12}(t))$

$= \prod_{i=1}^{c} (\frac{\nu_i \xi(t) + n_{i,0}}{\alpha\xi(t)+\beta})^{\nu_i}$

$= \frac{\prod_{i=1}^{c}(\nu_i\xi(t)+n_{i,0})^{\nu_i}}{(\alpha\xi(t)+\beta)^{\alpha}}$

$= G_\gamma(\xi(t))$

where $G_\gamma(x) = \frac{\prod_{i=1}^{c}(\nu_i x + n_{i,0})^{\nu_i}}{(\alpha x+\beta)^{\alpha}}$

We have that $\xi(0) = 0$, and, as we can assume that $\beta > 0$, we have that;

$G'_\gamma(0) = \frac{\sum_{i=1}^{c} \nu_i^2 n_{i,0}^{\nu_i - 1}(\prod_{j\neq i} n_{j,0}^{\nu_j})}{\beta^{\alpha}} - \frac{\alpha^2 \prod_{j=1}^{c} n_{j,0}^{\nu_j}}{\beta^{\alpha+1}}$

$= \frac{1}{\beta^{\alpha+1}}(\beta(\sum_{i=1}^{c} \nu_i^2 n_{i,0}^{\nu_i-1}(\prod_{j\neq i} n_{j,0}^{\nu_j}) - \alpha^2 \prod_{j=1}^{c} n_{j,0}^{\nu_j}))$

$= \frac{\prod_{j=1}^{c} n_{j,0}^{\nu_j}}{\beta^{\alpha+1}}(\beta \frac{\sum_{i=1}^{c}\nu_i^2}{n_{i,0}} - \alpha^2)$

$= \frac{\prod_{j=1}^{c} n_{j,0}^{\nu_j}}{\beta^{\alpha+1}}(n_{init} \frac{\sum_{i=1}^{c}\nu_i^2}{n_{i,0}} - \alpha^2)$

$= \frac{\prod_{j=1}^{c} n_{j,0}^{\nu_j}}{\beta^{\alpha+1}}(\sum_{i=1}^{c} \frac{\nu_i^2}{x_{i,init}} - \alpha^2)$

$= \frac{\prod_{j=1}^{c} (\frac{n_{j,0}}{n_{init}})^{\nu_j}}{\beta^{\alpha+1-\alpha}}(\sum_{i=1}^{c} \frac{\nu_i^2}{x_{i,init}} - \alpha^2)$

$= \frac{\prod_{j=1}^{c} (x_{j,0})^{\nu_j}}{\beta}(\sum_{i=1}^{c} \frac{\nu_i^2}{x_{i,init}} - \alpha^2)$

$= \frac{Q(\gamma_{12}(0))}{\beta}(\sum_{i=1}^{c} \frac{\nu_i^2}{x_{i,init}} - \alpha^2)$

so that;

$G'_\gamma(0) = 0$ iff $\sum_{i=1}^{c} \frac{\nu_i^2}{x_{i,init}} - \alpha^2 = 0$

For water electrolysis, with $0 \leq x_{init} \leq 1$, we have that;

$\sum_{i=1}^{c} \frac{\nu_i^2}{x_{i,init}} - \alpha^2 \geq \sum_{i=1}^{c} \nu_i^2 - \alpha^2 = 9 - 1 - 8 > 0$

By the inverse function theorem, we can invert G_γ locally, to obtain that $\xi(t) = (G_\gamma^{-1} \circ Q)(\gamma_{12}(t))$. Then;

$$\xi'(0) = (G_\gamma^{-1})'|_{Q(T_0,P_0)} grad(Q)(T_0, P_0) \cdot \gamma_{12}'(0)$$

$$= \frac{grad(Q)(T_0,P_0)\cdot\gamma_{12}'(0)}{G_\gamma'(0)}$$

$$= grad(Q)(T_0, P_0) \cdot \gamma_{12}'(0) \frac{\beta}{Q(\gamma_{12}(0))} \frac{1}{\sum_{i=1}^c \frac{\nu_i^2}{x_{i,init}} - \alpha^2}$$

where $\gamma_{12}(0) = (T_0, P_0)$.

As $\beta > 0$, $Q > 0$, see Lemma 7.2, $\frac{1}{\sum_{i=1}^c \frac{\nu_i^2}{x_{i,init}} - \alpha^2} > 0$, the above calculation makes it clear that, for water electrolysis, or for reactions with $\sum_{i=1}^c \nu_i^2 - \alpha^2 > 0$, $\xi'(0)$ is maximised when $\gamma_{12}'(0)$ points in the direction of $grad(Q)(T_0, P_0)$, with a positive rate of reaction, and minimised when $\gamma_{12}'(0)$ points against the direction of $grad(Q)(T_0, P_0)$, with a negative rate of reaction. The above calculation also makes it clear in these cases, that for a feasible path, we have that $\beta(t) > 0$, $Q(t) > 0$, $\frac{1}{\sum_{i=1}^c \frac{\nu_i^2}{x_i(t)} - \alpha^2} > 0$, so that $\xi'(t)$ is always finite, and we cannot pass through a point of ramification on the surface defined by $G_\gamma(\xi) = Q(T, P)$.

In either case, we, therefore, have to solve the paired differential equation;

$$\frac{dT}{dt} = \frac{-(\epsilon(P(t)-P^\circ)-\epsilon(T(t),P(t)))-T(t)\epsilon_T(T(t),P(t))}{RT(t)^2} e^{\frac{\epsilon(P(t)-P^\circ)-\epsilon(T(t),P(t))}{RT(t)}}$$

$$\frac{dP}{dt} = \frac{\epsilon-\epsilon_P(T(t),P(t))}{RT(t)} e^{\frac{\epsilon(P(t)-P^\circ)-\epsilon(T(t),P(t))}{RT(t)}}$$

so that;

$$\frac{dP}{dT} = \frac{\frac{dP}{dt}}{\frac{dT}{dt}}$$

$$= \frac{\frac{\epsilon-\epsilon_P(T,P)}{RT} e^{\frac{\epsilon(P-P^\circ)-\epsilon(T,P)}{RT}}}{\frac{-(\epsilon(P-P^\circ)-\epsilon(T,P))-T\epsilon_T(T,P)}{RT^2} e^{\frac{\epsilon(P-P^\circ)-\epsilon(T,P)}{RT}}}$$

$$= \frac{\frac{\epsilon-\epsilon_P(T,P)}{RT}}{\frac{-(\epsilon(P-P^\circ)-\epsilon(T,P))-T\epsilon_T(T,P)}{RT^2}}$$

$$= \frac{T(\epsilon-\epsilon_P(T,P))}{\epsilon(T,P)-\epsilon(P-P^\circ)-T\epsilon_T(T,P)}$$

If $\epsilon(T,P) = 0$, $\epsilon \neq 0$, then $\epsilon_T(P,T) = \epsilon_P(T,P) = 0$ and;

$\frac{dP}{dT} = \frac{T\epsilon}{-\epsilon(P-P^\circ)}$

$= -\frac{T}{(P-P^\circ)}$

Separating variables, we obtain that;

$(P - P^\circ)dP = -TdT$

which has an implicit solution given by;

$\int (P - P^\circ)dP = -\int TdT$

$(P - P^\circ)^2 = -T^2 + c$

for $c \in \mathcal{R}$. By a result due to [3], we have that these implicit solutions are integral curves for $grad(Q)$ as required.

The calculation of $grad(Q)$ when $\epsilon = 0$ is again a simple application of the chain rule. As before, we compute;

$\frac{\partial P}{\partial T} = -\frac{T\epsilon_P(T,P)}{\epsilon(T,P)-T\epsilon_T(T,P)}$

□

Remarks 3.7. *The fact that, in the case $\epsilon(P) = 0$, the paths of maximal reaction depend on an arbitrary choice of P° suggest that some approximation is needed in the formula;*

$\mu_i(T,P) = \mu_i^\circ(T) + RTlog(x_i(T,P))$

for ideal solutions. Of course, once P° is fixed, $\epsilon(P)$ depends on this choice of P° as well.

Lemma 3.8. *Using the notation of Lemma 3.6, for reactions with $\sum_{i=1}^{c} \nu_i^2 - \alpha^2 > 0$, given two points (T_0, P_0), (T_1, P_1), in the temperature/pressure plane, and an initial condition of molar amounts $\{n_{i,0} : 1 \leq i \leq c\}$ such that;*

$\prod_{i=1}^{c} x_{i,0}^{\nu_i} = Q(T_0, P_0)$ $(*)$

any two feasible paths connecting these points yield the same amount of substance, and given a path γ in the temperature pressure plane between these points, there exists a feasible path connecting them, and a unique feasible path λ with $pr_{12}(\lambda) = \gamma$, for given initial condition of molar amounts, satisfying $(*)$.

In the case of water electrolysis, we can determine the branch passing through $(0, T_0, P_0)$, and we can determine the error terms and chemical potentials, once the initial condition of molar amounts at (T, P°) is known. In water electrolysis we can minimise the energy used to create substance between two points, using Lagrangian methods.

Proof. The existence of feasible paths between two points in the temperature pressure plane is proved above. As explained in Lemma 3.6, feasible paths avoid the ramification locus defined by $G_\gamma(\xi) = Q(T, P)$, so intuitively a path in the temperature pressure plane can only have one continuous lifting, passing through $(0, T_0, P_0)$, to the surface defined by $G_\gamma(\xi) = Q(T, P)$, for a given initial condition. Alternatively, by the chain rule, we have that;

$$G'_\gamma(\xi)\xi' = \bigtriangledown(Q)(T, P) \cdot \gamma'_{12} \ (WW)$$

so that;

$$\xi(t_0) = \int_0^{t_0} \frac{\bigtriangledown(Q)(T,P)\cdot\gamma'_{12}}{G'_\gamma(\xi)(t)} dt \ (VV)$$

and we want to maximise (VV) subject to the constraint;

$$G_\gamma(\xi(t)) = Q(\gamma_{12}(t)) \ (A)$$

Letting $\gamma_{12}(t) = (T(t), P(t))$, we introduce the Lagrangian;

$$L(t, T, P, \xi, T', P') = F(t, T, P, \xi, T', P') + \mu(t)(G_\gamma(\xi(t)) - Q(T(t), P(t)))$$

where;

$$F(t, T, P, \xi, T', P') = \frac{\frac{\partial Q}{\partial T}(T,P)T' + \frac{\partial Q}{\partial P}(T,P)P'}{G'_\gamma(\xi)}$$

and μ is an auxiliary function to be determined. Then, Euler's equations are given by;

$(i).\ \frac{\partial L}{\partial T} - \frac{d}{dt}\frac{\partial L}{\partial T'} = 0$

$(ii).\ \frac{\partial L}{\partial P} - \frac{d}{dt}\frac{\partial L}{\partial P'} = 0$

$(iii).\ \frac{\partial L}{\partial \xi} - \frac{d}{dt}\frac{\partial L}{\partial \xi'} = 0$

We have that;

$\frac{\partial L}{\partial T} - \frac{d}{dt}\frac{\partial L}{\partial T'}$

$= \frac{\partial F}{\partial T} - \frac{d}{dt}\frac{\partial F}{\partial T'} - \mu(t)\frac{\partial Q}{\partial T}$

$= \frac{\frac{\partial^2 Q}{\partial^2 T}T' + \frac{\partial^2 Q}{\partial T \partial P}P'}{G'_\gamma(\xi)} - \frac{d}{dt}(\frac{\frac{\partial Q}{\partial T}}{G'_\gamma(\xi)}) - \mu(t)\frac{\partial Q}{\partial T}$

$= \frac{\frac{\partial^2 Q}{\partial^2 T}T' + \frac{\partial^2 Q}{\partial T \partial P}P'}{G'_\gamma(\xi)} - \frac{\frac{\partial^2 Q}{\partial T^2}T' + \frac{\partial^2 Q}{\partial T \partial P}P'}{G'_\gamma(\xi)} + \frac{G''_\gamma(\xi)\xi'\frac{\partial Q}{\partial T}}{G'_\gamma(\xi)^2} - \mu(t)\frac{\partial Q}{\partial T}$

$= \frac{G''_\gamma(\xi)\xi'\frac{\partial Q}{\partial T}}{G'_\gamma(\xi)^2} - \mu(t)\frac{\partial Q}{\partial T}$

so that $\mu(t) = \frac{G''_\gamma(\xi)\xi'}{G'_\gamma(\xi)^2}$, and;

$\frac{\partial L}{\partial P} - \frac{d}{dt}\frac{\partial L}{\partial P'}$

$= \frac{\partial F}{\partial P} - \frac{d}{dt}\frac{\partial F}{\partial P'} - \mu(t)\frac{\partial Q}{\partial P}$

$= \frac{\frac{\partial^2 Q}{\partial T \partial P}T' + \frac{\partial^2 Q}{\partial P^2}P'}{G'_\gamma(\xi)} - \frac{d}{dt}(\frac{\frac{\partial Q}{\partial P}}{G'_\gamma(\xi)}) - \mu(t)\frac{\partial Q}{\partial P}$

$= \frac{\frac{\partial^2 Q}{\partial T \partial P}T' + \frac{\partial^2 Q}{\partial^2 P}P'}{G'_\gamma(\xi)} - \frac{\frac{\partial^2 Q}{\partial T \partial P}T' + \frac{\partial^2 Q}{\partial^2 P}P'}{G'_\gamma(\xi)} + \frac{G''_\gamma(\xi)\xi'\frac{\partial Q}{\partial P}}{G'_\gamma(\xi)^2} - \mu(t)\frac{\partial Q}{\partial P}$

$= \frac{G''_\gamma(\xi)\xi'\frac{\partial Q}{\partial P}}{G'_\gamma(\xi)^2} - \mu(t)\frac{\partial Q}{\partial P}$

so that $\mu(t) = \frac{G''_\gamma(\xi)\xi'}{G'_\gamma(\xi)^2}$ again. Finally;

$\frac{\partial L}{\partial \xi} - \frac{d}{dt}\frac{\partial L}{\partial \xi'}$

$= \frac{\partial F}{\partial \xi} - \frac{d}{dt}\frac{\partial F}{\partial \xi'} + \mu(t)G'_\gamma(\xi)$

$= \frac{\partial F}{\partial \xi} + \mu(t)G'_\gamma(\xi)$

$= -\frac{G''_\gamma(\xi)(\frac{\partial Q}{\partial T}(T,P)T' + \frac{\partial Q}{\partial P}(T,P)P')}{G'_\gamma(\xi)^2} + \mu(t)G'_\gamma(\xi)$

so that;

$\frac{G''_\gamma(\xi)\xi'}{G'_\gamma(\xi)} = \frac{G''_\gamma(\xi)\bigtriangledown(Q)\cdot\gamma'_{12}}{G'_\gamma(\xi)^2}$

$\xi' = \frac{\bigtriangledown(Q)\cdot\gamma'_{12}}{G'_\gamma(\xi)}$

which is (WW). The method gives no information. We can overcome this obstacle, in the general reaction case, by using Newton's theorem, but there is an issue with computing the branches explicitly in terms of (T, P). In the case of water electrolysis $2H_2 + O_2 \to 2H_20$, we can use the cubic formula, as denoting H_2 by substance 1, O_2 by substance 2, H_2O by substance 3;

$\prod_{i=1}^3 x_i^{\nu_i} = Q(T, P)$

iff $\frac{(n_{10}-2\xi)^{-2}(n_{20}-\xi)^{-1}(n_{30}+2\xi)^2}{(n_0-\xi)^{-1}} = Q(T, P)$

iff $a\xi^3 + b\xi^2 + c\xi + d = 0$

where;

$a = 4(Q(T, P) - 1)$

$b = 4n_0 - 4n_{30} - Q(T, P)(4n_{10} + 4n_{20})$

$c = 4n_0n_{30} - n_{30}^2 + Q(T, P)(4n_{10}n_{20} + n_{10}^2)$

$d = n_{30}^2n_0 - Q(T, P)n_{10}^2n_{20}$

$n_0 = n_{10} + n_{20} + n_{30}$, $\{n_{10}, n_{20}, n_{30}\}$ are the initial molar amounts, satisfying;

$\prod_{i=1}^3 x_{i0}^{\nu_i} = Q(T_0, P_0)$

The values $\Delta_0 = b^2 - 3ac$ and $\Delta_1 = 2b^3 - 9abc + 27ad^2$ are given by;

$\Delta_0 = Q^2[4n_{10}^2 + 16n_{20}^2 - 16n_{01}n_{02}]$

$+Q[-32n_0n_{10} - 32n_0n_{20} - 48n_0n_{30} + 12n_{10}^2 + 12n_{30}^2 + 48n_{10}n_{20}$

$+32n_{10}n_{30} + 32n_{20}n_{30}]$

$+[16n_0^2 + 4n_{30}^2 + 16n_0n_{30}]$

$\Delta_1 = Q^3[-8(n_{10} + n_{20})^3 + 576n_{30}(n_{10} + n_{20})^2 + \frac{108n_{30}^4n_0^2}{Q(T_0,P_0)}]$

$+Q^2[24(n_{10} + n_{20})^3 - 576n_{30}(n_{10} + n_{20})^2 - \frac{108n_{30}^4n_0^2}{Q^2(T_0,P_0)} - \frac{216n_{30}^4n_0^2}{Q(T_0,P_0)}]$

$+Q[-24(n_{10} + n_{20})^3 - 576n_{30}(n_{10} + n_{20})^2 + 108n_{30}^4n_0^2 + \frac{116n_{30}^4n_0^2}{Q(T_0,P_0)}]$

$+[8(n_{10} + n_{20})^3 + 576n_{30}(n_{10} + n_{20})^2 - 108n_{30}^4n_0^2]$

Letting $C = (\frac{\Delta_1 +/- \sqrt{\Delta_1^2 - 4\Delta_0^3}}{2})^{\frac{1}{3}}$, $(*)$, we obtain a real branch, by setting $\xi = -\frac{1}{3a}(b + C + \frac{\Delta_0}{C})$ for the appropriate square root in $(*)$. However, in practice, this method is cumbersome and an alternative approximation is found below.

Denoting the theoretical branch through $(0, T_0, P_0)$ as $f(T, P, n_{10}, n_{20}, n_{30})$, we can then in principle determine the chemical potentials $f_i(T, P)$ by;

$f_i(T, P) = f_i(T, P^\circ) + RTln(x_i)$

$= f_i(T, P^\circ) + RTln(\frac{n_{i0}+\nu_i\xi}{n_0+\alpha\xi})$

$= f_i(T, P^\circ) + RTln(\frac{n_{i0}+\nu_i f(T,P,n_{10},n_{20},n_{30})}{n_0+\alpha f(T,P,n_{10},n_{20},n_{30})})$

and use the formula;

$\xi(t_0) = \int_0^{t_0} \bigtriangledown(f) \cdot \gamma'_{12} dt$

to compute the amount of substance formed along a reaction path. This makes it clear that in water electrolysis, no substance is formed in a loop, although there may be paths with a higher yield of reaction. We can use the Lagrangian method to minimise the energy involved in water electrolysis, using the functional;

$E(t_0) = \int_0^{t_0} V(t)I(t)dt$

$= \int_0^{t_0} (V^\circ(t, T, P) - \frac{RTln(Q)(T,P,t)}{4F}) 4F \bigtriangledown (f) \cdot \gamma'_{12} dt$

which is not an exact differential.

Once the amount of substance ξ is determined, we obtain a feasible path by setting $n_i = n_{i,0} + \nu_i \xi$, $1 \leq i \leq 3$. Knowledge of the branch $f(T, P, n_{10}, n_{20}, n_{30})$ also allows us to determine the molar amounts $n_i(T, P^\circ)$, $1 \leq i \leq 3$ which appear as error terms for Q, if they are undetermined, and not all the substances obey Raoult's law (ideal solution). Namely, for $1 \leq i \leq 3$;

$$n_i(T, P^\circ) = n_{i0} + \nu_i f(T, P^\circ, n_{10}, n_{20}, n_{30}, n_1(T, P^\circ), n_2(T, P^\circ), n_3(T, P^\circ))$$

(FF)

so that, differentiating, for $1 \leq i \leq 3$;

$$n_i'(T, P^\circ) = \nu_i [\frac{\partial f}{\partial T} + \sum_{j=1}^{3} \frac{\partial f}{\partial y_j} n_j'(T, P^\circ)]$$

which has a unique solution given $\{n_1(T_0, P^\circ), n_2(T_0, P^\circ), n_3(T_0, P^\circ)\}$, taking (T_0, P°) as the base point, by Peano's existence theorem, assuming $\prod_{i=1}^{3} x_{i,0}^{\nu_i} = Q(T_0, P^\circ)$ is satisfied. This gives a solution of (FF), as, then;

$$n_i(T, P^\circ) = n_{i0} + \nu_i f(T, P^\circ, n_{10}, n_{20}, n_{30}, n_1(T, P^\circ), n_2(T, P^\circ), n_3(T, P^\circ))$$

$+c$

with $c = 0$, as automatically, by the property of the branch;

$$n_i(T_0, P^\circ) = n_{i0} + \nu_i f(T_0, P^\circ, n_{10}, n_{20}, n_{30}, n_1(T_0, P^\circ), n_2(T_0, P^\circ), n_3(T_0, P^\circ))$$

Using the fact that $\mu_i = \mu_i^\circ + RTlog(x_i) + \epsilon_i(T, P)$, we know that the error terms $\epsilon_i(T, P^\circ)$ are of the form $-RTlog(x_i(T, P^\circ)$, (BC), so that, if $\epsilon_i(T, P)$ is not known explicitly as a function of T and P;

$$Q(T, P) = Q'(T, P) e^{\frac{-\epsilon(T,P)}{RT}}$$

$$= Q'(T, P) e^{\frac{-\sum_{i=1}^{c} \nu_i \epsilon_i(T,P)}{RT}}$$

$$= Q'(T, P) \prod_{i=1}^{c} x_i^{\nu_i}$$

where $Q'(T,P)$ has been determined with $Q'(T,P^\circ)=1$.

The initial condition of the equation $\prod_{i=1}^{c} x_i^{\nu_i}(T,P)$ at (T_0,P°) reduces to the equation;

$$\prod_{i=1}^{c} x_{i,0}^{\nu_i} = Q'(T,P)\prod_{i=1}^{c} x_{i,0}^{\nu_i}$$

which is a tautology, so we are free to choose the initial molar amounts $\{n_{i,0} : 1 \leq i \leq c\}$. However, in the case when all substances obey Raoult's law, we obtain the equation $\prod_{i=1}^{c} x_i^{\nu_i} = Q(T,P^\circ)\prod_{i=1}^{c} x_i^{\nu_i}$, with $Q(T,P^\circ)=1$ everywhere on $P=P^\circ$, so the error terms can be arbitrary along $P=P^\circ$. Otherwise, the equation does then lead to a determination of $x_i(T,P^\circ)$, for $T \neq T_0$, as explained above, provided we use the initial conditions at (T_0,P°), when formulating $\prod_{i=1}^{c} x_i^{\nu_i}(T,P)$ as a rational function of ξ with coefficients in $\{n_{i,0} : 1 \leq i \leq c\}$. If, on the other hand, $\epsilon_i(T,P)$ is known explicitly as a function of T and P, it determines, by (BC), $x_i(T,P^\circ)$, and, moreover, the functions $g_i(T) = x_i(T,P^\circ)$ will be continuous as a function of T. For a feasible path γ, the cover determined by;

$$x_i = \tfrac{n_{i0}+\nu_i\xi}{n_0+\alpha\xi} \text{ and } G_\gamma(\xi) = Q(T,P)$$

is finite, once the undetermined coefficients $x_j(T,P^\circ)$ $1 \leq j \leq p$, $j \neq i$, have been found by the above method. Moreover, the cover will be unramified along the path γ, as $n(t) \neq 0$, so that, considering a path along $P=P^\circ$, defining;

$$h(T) = x_i(T,P^\circ) = \tfrac{n_{i0}+\nu_i f(T,P^\circ,\overline{n}_0)}{n_0+\alpha f(T,P^\circ,\overline{n}_0)}$$

where $\overline{n}_0$ are the initial molar amounts, both determined and undetermined, by uniqueness of lifts and continuity, we must have that $g(T)=h(T)$, so the theory is consistent.

□

Lemma 3.9. *For water electrolysis, and with Raoult's law for the solvent and Henry's law for the solutes, we have, given a feasible path γ, the Arrhenius type formula for the rate of reaction;*

$$\xi'(t) \simeq DC_\gamma e^{\frac{-E_a}{RT}}[H_2]^2[O_2]V$$

where D is a constant, C_γ is a constant depending on $\gamma'(t)$ and (T,P), E_a is the activation energy $\epsilon(P-P^0)$, $[H_2]$ is the concentration of hydrogen, $[O_2]$ is the concentration of oxygen, V is the volume of the mixture.

For a feasible path, beginning at (T_0,P_0) and ending at (T,P), we have the integrated rate law for the substance ξ formed;

$$\frac{-2x}{(x_1-2x_2)(x_1-2x)x_1}+\frac{1}{(x_1-2x_2)^2}ln(\frac{x_1-2x}{x_2-x}\frac{x_2}{x_1})\simeq\frac{A}{3}(Q_1(T,P)-Q_1(T_0,P_0))$$

where $\{x_1,x_2\}$ are the initial concentrations of hydrogen and oxygen, $\{x_1,x_2\}$, $Q_1=e^{\frac{\epsilon(P-P^\circ)}{RT}}$, A is a constant, $x=\frac{\xi}{n}$.

For water electrolysis, we have, given a feasible path γ, the Arrhenius type formula for the rate of reaction;

$$\xi'(t)\simeq D_\gamma e^{\frac{-E_a}{RT}}[H_2]^2[O_2]V$$

where D_γ is a constant depending on $\gamma'(t)$ and (T,P), E_a is the activation energy $\epsilon(P-P^0)$, $[H_2]$ is the concentration of hydrogen, $[O_2]$ is the concentration of oxygen, V is the volume of the mixture.

For a feasible path, beginning at (T_0,P_0) and ending at (T,P), we have the integrated rate law for the substance ξ formed;

$$\frac{-2x}{(x_1-2x_2)(x_1-2x)x_1}+\frac{1}{(x_1-2x_2)^2}ln(\frac{x_1-2x}{x_2-x}\frac{x_2}{x_1})\simeq\frac{1}{3}(Q_0(T,P)-Q_0(T_0,P_0))$$

see [8]*, where $\{x_1,x_2\}$ are the initial concentrations of hydrogen and oxygen, $x=\frac{\xi}{n}$, and;*

$$Q_0(T,P)=e^{\frac{\epsilon(P-P^\circ)}{RT}}(\frac{\delta_1(T,P^\circ)}{\delta_1(T,P)})^2(\frac{\delta_2(T,P^\circ)}{\delta_2(T,P)})(\frac{P^\circ}{k_1\gamma_1(T,P)})^2(\frac{P^\circ}{k_2\gamma_2(T,P)})(\frac{\gamma_3(T,P)}{\gamma_3(T,P^\circ)})^2$$

Proof. In general, the error terms from Raoult's law (for the solvent) will be undetermined, while the error terms for Henry's law (the solutes) will be determined. Equivalently, in water electrolysis, we are free to choose the initial amount n_{30} of solvent, and then the molar amounts $\{n_{10},n_{20}\}$ of the solutes are determined at (T_0,P°), if $0\leq x_1(T_0,P^\circ)<1$, $0\leq x_2(T_0,P^\circ)<1$.

Explicitly, for water electrolysis, assuming Raoult's law and Henry's law, using Lemma **??**, we have that;

$Q(T,P) = \frac{P^\circ}{P} e^{\frac{\epsilon(P-P^\circ)-\gamma(T,P)}{RT}}$

where $\gamma(T,P)$ is the error term;

$\sum_{i=1}^{3} \nu_i \gamma_i(T,P)$

$\gamma_1(T,P) = RTln(\frac{k_1}{P^\circ})$ (solute H_2)

$\gamma_2(T,P) = RTln(\frac{k_2}{P^\circ})$ (solute O_2)

$\gamma_3(T,P) = -RTln(x_3(T,P^\circ))$ (solvent H_2O) (AA)

see Definition 6.1, footnote 5, and the paper [13] for the solvent calculation.

If $p(T,P,\xi,n_{01}n_{02},n_{03})$ is the polynomial;

$a\xi^3 + b\xi^2 + c\xi + d = 0$

given above, then as $p(T,P,\xi,n_{01}n_{02},n_{03}) = 0$, for a feasible path γ, we have that;

$\theta_\gamma(t,\xi(t)) = 0$

where

$\theta_\gamma(t,\xi) = p(\gamma_1(t),\gamma_2(t),\xi,n_{01}n_{02},n_{03})$

so that, differentiating with respect to t;

$\frac{\partial\theta_\gamma}{\partial t} + \frac{\partial\theta_\gamma}{\partial\xi}\xi' = 0$

$\xi' = -\frac{\frac{\partial\theta_\gamma}{\partial t}}{\frac{\partial\theta_\gamma}{\partial\xi}}$

$\xi(0) = 0$

can be solved by a step by step Matlab calculation, though no explicit solution seems easy to find.

We have that;

$\frac{\partial \theta_\gamma}{\partial t}|_0 = (\frac{\partial a}{\partial t}\xi^3 + \frac{\partial b}{\partial t}\xi^2 + \frac{\partial c}{\partial t}\xi + \frac{\partial d}{\partial t})|_0$

$= \frac{\partial d}{\partial t}|_0$

$= \frac{\partial (n_{30}^2 n_0 - Q(T(t),P(t)) n_{10}^2 n_{20})}{\partial t}|_0$

$= -n_{10}^2 n_{20} \bigtriangledown Q \centerdot \gamma_{12}'(0)$

$\frac{\partial \theta_\gamma}{\partial \xi}|_0 = (3a\xi^2 + 2b\xi + c)|_0$

$= c(0)$

$= 4n_0 n_{30} - n_{30}^2 + Q(\gamma_{12}(0))(4n_{10}n_{20} + n_{10}^2)$

so that;

$\xi'(0) = -\frac{\frac{\partial \theta_\gamma}{\partial t}|_0}{\frac{\partial \theta_\gamma}{\partial \xi}|_0}$

$= \frac{n_{10}^2 n_{20} \bigtriangledown Q \centerdot \gamma_{12}'(0)}{4n_0 n_{30} - n_{30}^2 + Q(\gamma_{12}(0))(4n_{10}n_{20} + n_{10}^2)}$

Noting that with $n_{10} << n_{30}$, $4n_{10}n_{20} + n_{10}^2 << 4n_0 n_{30} - n_{30}^2$, we can use Newton's theorem to expand this as;

$\xi'(0) = \frac{n_{10}^2 n_{20}}{4n_0 n_{30} - n_{30}^2} \bigtriangledown Q \centerdot \gamma_{12}'(0) \sum_{n=0}^{\infty} (-1)^n Q^n (\frac{4n_{10}n_{20} + n_{10}^2}{4n_0 n_{30} - n_{30}^2})^n$

$\simeq \frac{n_{10}^2 n_{20}}{4n_0 n_{30} - n_{30}^2} \bigtriangledown Q \centerdot \gamma_{12}'(0)$

$\simeq \frac{x_{10}^2 x_{20} n_0}{3} \bigtriangledown Q \centerdot \gamma_{12}'(0)$ (FF)

which, given the form of Q, is an Arrhenius like formula, see also following remark, but Q still contains error terms which are undetermined for the solvent.

More specifically, including the error term for the solvent which we assume obeys Raoult's law, we have that;

$\frac{(n-\xi)(n_3+2\xi)^2}{(n_1-2\xi)^2(n_2-\xi)} = Q_0 x_3^2$

$= Q_0 \frac{(n_3+2\xi)^2}{(n-\xi)^2}$

where Q_0 only depends on temperature and pressure, and the feasible path along $P = P^\circ$, so that, cancelling terms;

$(n-\xi)^3 = Q_0(n_1-2\xi)^2(n_2-\xi)$

so that, applying the method above, and using the fact that $n \simeq n_3$;

$\xi'(0) = \frac{-n_1^2 n_2 \bigtriangledown(Q_0)\centerdot\gamma'}{-3n^2+(n_1^2+4n_1n_2)Q_0}$

$\simeq \frac{x_1 x_2 n_1 \bigtriangledown(Q_0)\centerdot\gamma'}{3}$

Noting that, including error terms for the solutes, which we assume obey Henry's law with constants $\{k_1, k_2\}$, independent of temperature at P°, we have that, using (AA);

$Q_0 = e^{\frac{\epsilon(P-P^\circ)}{RT}}(\frac{P^\circ}{k_1})^2(\frac{P^\circ}{k_1})$

$= (\frac{P^\circ}{k_1})^2(\frac{P^\circ}{k_1})$

so that $\bigtriangledown(Q_0)\centerdot\gamma' = 0$ and, $\xi'(0) = 0$. It follows that the concentrations and molar amounts $\{x_1, x_2, x_3, n_1, n_2, n_3\}$ remain constant along $P = P^\circ$.

Then choosing an arbitrary path from (T_0, P°) with the quantities above determined along $P = P^\circ$, we have that;

$\frac{(n-\xi)(n_3+2\xi)^2}{(n_1-2\xi)^2(n_2-\xi)} = A\frac{P}{P^\circ}e^{\frac{\epsilon(P-P^\circ)}{RT}}\frac{n_3^2}{n^2}$

so that;

$n^2(n-\xi)(n_3+2\xi)^2 = AQ_1 n_3^2(n_1-2\xi)^2(n_2-\xi)$

and;

$\xi'(0) = \frac{A\bigtriangledown Q_1\centerdot\gamma' n_3^2 n_1^2 n_2}{(4nn_3-n_3^2)n^2+AQ_1(n_3^2n_1^2+4n_1n_2n_3^2)}$

$\simeq \frac{A \bigtriangledown Q_1 \centerdot \gamma' n_3^2 n_1^2 n_2}{n^2(4nn_3 - n_3^2)}$

so that, with $n \simeq n_3$,

$\xi'(0) \simeq \frac{A}{3} \bigtriangledown Q_1 \centerdot \gamma' x_1^2 x_2 n$

and, repeating the calculation, with the feasible path evaluated at t, and the constants k_i assumed independent of temperature and pressure;

$\xi'(t) \simeq \frac{A}{3} \bigtriangledown Q_1 \centerdot \gamma' x_1^2 x_2 n$ (SV)

where $Q_1 = e^{\frac{\epsilon(P-P^\circ)}{RT}}$.

so that;

$\bigtriangledown Q_1 \centerdot \gamma' = C_\gamma e^{\frac{\epsilon(P-P^\circ)}{RT}}$

$= C_\gamma e^{\frac{-E_a}{RT}}$

$\xi'(t) \simeq A C_\gamma e^{\frac{-E_a}{RT}} x_1^2 x_2 n$

$= B C_\gamma e^{\frac{-E_a}{RT}} [H_2]^2 [O_2] n$

$= D C_\gamma e^{\frac{-E_a}{RT}} [H_2]^2 [O_2] V$

where V is volume, which agrees closely with the Arrhenius formula for this type of reaction.

Rearranging (SV), we have that;

$\xi'(t) \frac{(n-\xi(t))^2}{(n_1 - 2\xi(t))^2 (n_2 - \xi(t))} \simeq \frac{A}{3} \bigtriangledown Q_1 \centerdot \gamma'$

where $\{n, n_1, n_2\}$ are the initial conditions, so that, separating variables;

$\int d\xi \frac{(n-\xi)^2}{(n_1 - 2\xi)^2 (n_2 - \xi)} \simeq \int \frac{A}{3} \bigtriangledown Q_1 \centerdot \gamma' dt$ (VT)

Using partial fractions, we have that;

$\frac{(n-\xi)^2}{(n_1 - 2\xi)^2 (n_2 - \xi)} = \frac{A}{(n_1 - 2\xi)^2} + \frac{B}{(n_1 - 2\xi)} + \frac{C}{(n_2 - \xi)}$ (VS)

$= \frac{A(n_2-\xi)+B(n_1-2\xi)(n_2-\xi)+C(n_1-2\xi)^2}{(n_1-2\xi)^2(n_2-\xi)}$

so that equating coefficients;

$(i)\ 2B + 4C = 1$

$(ii).\ -A - n_1B - 2n_2B - 4n_1C = -2n$

$(iii).\ An_2 + Bn_1n_2 + Cn_1^2 = n^2$

From (i), we obtain that $B = \frac{1}{2} - 2C.$ and substituting into $(ii), (iii)$, we have that;

$(ii)'\ -A - (n_1 + 2n_2)(\frac{1}{2} - 2C) - 4n_1C = -2n$

$(iii)'\ An_2 + n_1n_2(\frac{1}{2} - 2C) + Cn_1^2 = n^2$

It follows that, from $(ii)'$

$A = 2n - (n_1 + 2n_2)(\frac{1}{2} - 2C) - 4n_1C\ (VW)$

and substituting into $(iii)'$;

$[2n - (n_1 + 2n_2)(\frac{1}{2} - 2C) - 4n_1C]n_2 + n_1n_2(\frac{1}{2} - 2C) + Cn_1^2 = n^2$

Rearranging, using $n \simeq n_3$, we obtain that;

$C = \frac{n^2-2n_1n_2+n_2^2}{n_1^2-4n_1n_2+4n_2^2}$

$\simeq \frac{n^2}{(n_1-2n_2)^2}$

$= \frac{1}{(x_1-2x_2)^2}$

and then;

$B = \frac{1}{2} - 2C = \frac{\frac{n_1^2}{2}+2n_1n_2-2n^2}{n_1^2-4n_1n_2+4n_2^2}$

$\simeq \frac{-2n^2}{(n_1-2n_2)^2}$

$= -\frac{2}{(x_1-2x_2)^2}$

From (VW);

$A \simeq 2n - (n_1 + 2n_2)(\frac{-2n^2}{(n_1-2n_2)^2}) - 4n_1(\frac{n^2}{(n_1-2n_2)^2})$

$= 2n + \frac{2(n_1+2n_2)-4n_1}{(x_1-2x_2)^2}$

$= n(2 + \frac{4x_2-2x_1}{(x_1-2x_2)^2})$

$= n(\frac{2x_1-4x_2-2}{x_1-2x_2})$

$\simeq \frac{-2n}{x_1-2x_2}$

and then, from $(VT), (VS)$;

$\frac{-n}{(x_1-2x_2)(n_1-2\xi)} + \frac{1}{(x_1-2x_2)^2} ln(\frac{n_1-2\xi}{n_2-\xi}) \simeq \frac{A}{3}(Q_1(T,P) - Q_1(T_0,P_0)) - \frac{1}{x_1(x_1-2x_2)}$

$+ \frac{1}{(x_1-2x_2)^2} ln(\frac{x_1}{x_2})$

so that, letting $x = \frac{\xi}{n}$, we obtain;

$\frac{-1}{(x_1-2x_2)(x_1-2x)} + \frac{1}{(x_1-2x_2)^2} ln(\frac{x_1-2x}{x_2-x}) \simeq \frac{A}{3}(Q_1(T,P) - Q_1(T_0,P_0)) - \frac{1}{x_1(x_1-2x_2)}$

$+ \frac{1}{(x_1-2x_2)^2} ln(\frac{x_1}{x_2})$

and rearranging again;

$\frac{-2x}{(x_1-2x_2)(x_1-2x)x_1} + \frac{1}{(x_1-2x_2)^2} ln(\frac{x_1-2x}{x_2-x}\frac{x_2}{x_1}) \simeq \frac{A}{3}(Q_1(T,P) - Q_1(T_0,P_0))$

which agrees closely with a formula given in [8].

In the case, where we do not assume Raoult's law for the solvent or Henry's law for the solutes, we have that;

$Q(T,P) = e^{\frac{\epsilon(P-P^\circ)-\gamma(T,P)}{RT}}$

where $\gamma(T,P)$ is the error term;

$\sum_{i=1}^{3} \nu_i \gamma_i(T,P)$

$\gamma_1(T,P) = RTln(\frac{\delta_1(T,P)}{\delta_1(T,P^\circ)}) + RTln(\frac{k_1\gamma_1(T,P)}{P^\circ})$ (solute H_2)

$\gamma_2(T,P) = RTln(\frac{\delta_2(T,P)}{\delta_2(T,P^\circ)}) + RTln(\frac{k_2\gamma_2(T,P)}{P^\circ})$ (solute O_2)

$\gamma_3(T,P) = RTln(\frac{\gamma_3(T,P)}{\gamma_3(T,P^\circ)}) - RTln(x_3(T,P^\circ))$ (solvent H_2O)

see Definition 8.1, footnote 6, Lemma **??** and the paper [13] for the solvent calculation.

Following the proof above, we have to recalculate Q_0 as;

$Q_0(T,P) = e^{\frac{\epsilon(P-P^\circ)}{RT}}(\frac{\delta_1(T,P^\circ)}{\delta_1(T,P)})^2(\frac{\delta_2(T,P^\circ)}{\delta_2(T,P)})(\frac{P^\circ}{k_1\gamma_1(T,P)})^2(\frac{P^\circ}{k_2\gamma_2(T,P)})(\frac{\gamma_3(T,P)}{\gamma_3(T,P^\circ)})^2$

so that;

$Q_0(T,P^\circ) = (\frac{P^\circ}{k_1\gamma_1(T,P^\circ)})^2(\frac{P^\circ}{k_2\gamma_2(T,P^\circ)})$

We assume that $\{\gamma_1,\gamma_2\}$, the deviations from Henry's law, do not vary much along the line $P = P^\circ$, in which case we can assume that $Q_0|_{P=P^\circ} = c$, and $\bigtriangledown Q_0 \centerdot \gamma' = 0$ for a path γ along $P = P^\circ$. We can then conclude above, that, for such a feasible path, $\xi'(0) = 0$ and the mole fractions and molar amounts $\{x_1,x_2,x_3,n_1,n_2,n_3\}$ remain constant along $P = P^\circ$. We then replace Q_1 in the proof above by $Q_0 = A(T,P)Q_1$, and calculate;

$\bigtriangledown Q_0 \centerdot \gamma' = Q_1 \bigtriangledown A \centerdot \gamma' + A \bigtriangledown Q_1 \centerdot \gamma'$

$\xi'(t) \simeq \frac{(Q_1 \bigtriangledown A \centerdot \gamma' + A \bigtriangledown Q_1 \centerdot \gamma')}{3}[H_2]^2[O_2]V$

$= D_\gamma e^{\frac{-E_a}{RT}}[H_2]^2[O_2]V$

where $D_\gamma(T,P)$ depends on the path γ.

The integrated rate law then becomes;

$\frac{-2x}{(x_1-2x_2)(x_1-2x)x_1} + \frac{1}{(x_1-2x_2)^2}ln(\frac{x_1-2x}{x_2-x}\frac{x_2}{x_1}) \simeq \frac{1}{3}(Q_0(T,P) - Q_0(T_0,P_0))$

where $x = \frac{\xi}{n}$

Alternatively, we can start with the rate law;

$\xi'(t) \simeq \frac{1}{3} \bigtriangledown (Q) \centerdot \gamma' x_1^2 x_2 n$

where $Q = Ae^{\frac{\epsilon(P-P^{\circ})}{RT}}$, A is a constant, and noting that;

$x_1^2 x_2 \simeq \frac{x_1^2 x_2}{x_3^2}$

$= \frac{1}{Q}$

for the fuel cell reaction, with a dilute solution, $x_3 \simeq 1$ and the definition of Q, we obtain;

$\xi'(t) \simeq \frac{1}{3} \bigtriangledown (Q) \cdot \gamma' \frac{n}{Q}$

$= \frac{1}{3} \bigtriangledown (ln(Q)) \cdot \gamma' n$

so that;

$\frac{\xi'}{(n_0 - \xi)} = \frac{1}{3} \bigtriangledown (ln(Q)) \cdot \gamma'$

and integrating along a feasible path between (T_0, P_0) and (T, P);

$ln(n_0 - \xi) - ln(n_0) = -\frac{1}{3}(ln(Q)(T, P) - ln(Q)(T_0, P_0))$

$= -\frac{1}{3} ln(\frac{Q(T,P)}{Q(T_0,P_0)})$

$= ln(\frac{n_0 - \xi}{n_0})$

so that;

$\frac{n_0 - \xi}{n_0} = (\frac{Q(T,P)}{Q(T_0,P_0)})^{\frac{-1}{3}}$

$n = n_0 - \xi = n_0(\frac{Q(T,P)}{Q(T_0,P_0)})^{\frac{-1}{3}}$ (CD)

$\xi = n_0[1 - (\frac{Q(T,P)}{Q(T_0,P_0)})^{\frac{-1}{3}}]$

and the rate law becomes;

$\xi' = \frac{1}{3} \bigtriangledown (ln(Q)) \cdot \gamma' n_0(\frac{Q(T,P)}{Q(T_0,P_0)})^{\frac{-1}{3}}$

By results of [13], we have that the energy $E(T, P, \gamma)$ liberated along a feasible path γ is given by;

$$E(T,P,\gamma) = \int_{\gamma,(T_0,P_0)}^{(T,P)} -(\lambda + \epsilon P + \beta T)\xi'$$

$$= \int_{\gamma,(T_0,P_0)}^{(T,P)} -(\lambda + \epsilon P + \beta T)\tfrac{1}{3} \bigtriangledown (ln(Q)) \centerdot \gamma' n_0 (\tfrac{Q(T,P)}{Q(T_0,P_0)})^{\frac{-1}{3}}$$

$$= -\tfrac{n_0}{3Q(T_0,P_0)^{\frac{-1}{3}}} \int_{\gamma,(T_0,P_0)}^{(T,P)} (\lambda + \epsilon P + \beta T) \bigtriangledown (ln(Q)) \centerdot \gamma' Q(T,P)^{\frac{-1}{3}}$$

$$= -\tfrac{An_0}{3Q(T_0,P_0)^{\frac{-1}{3}}} \int_{\gamma,(T_0,P_0)}^{(T,P)} (\lambda + \epsilon P + \beta T)(\tfrac{-\epsilon(P-P^\circ)T'}{RT^2} + \tfrac{\epsilon P'}{RT}) e^{\frac{-\epsilon(P-P^\circ)}{3RT}}$$

We want to minimise $E(T,P)$ and maximise $\xi(T,P)$. We have that $n = n_0 - \xi$, and ξ is negative for electrolysis.

Using the Nernst equation, which doesn't use error terms, we have that;

$$V_0 - V^\circ = -\tfrac{RT_0}{4F} ln(Q)$$

$$= -\tfrac{RT_0}{4F} \tfrac{\epsilon(P_0 - P^\circ)}{RT_0}$$

$$= -\tfrac{\epsilon}{4F}(P_0 - P^\circ)$$

□

Remarks 3.10. *Evaluation of the constants λ,β*

We have the data;

$\epsilon \simeq -4.96 \times 10^{-5}$

$\lambda \simeq \Delta H^\circ = -2.86 \times 10^5$

$F = 96500$

$R = 8.3145$

We can calculate β theoretically, using the formula;

$\beta = \tfrac{\Delta G^\circ(T) - \Delta H^\circ}{T}$

$= \tfrac{(\Delta H^\circ - T\Delta S^\circ) - \Delta H^\circ}{T}$

$= -\Delta S^\circ$

Alternatively, we can use the fact that;

$$V^\circ(T) = -\tfrac{1}{4F}\Delta G^\circ(T)$$

$$= -\tfrac{1}{4F}(\lambda + \beta T + \epsilon P^\circ)$$

so that, differentiating with respect to T;

$$\beta = -4F\tfrac{dV^\circ(T)}{dT}$$

We can perform a simple experiment with a glass of water, a multimeter and a thermometer to see how V° varies with the temperature T. The data is somewhat sporadic, but we performed the experiment three times and fitted the data of V° against T to three regression lines. We found values of β to be 385.34, 395.28 *and* 310.99*. We can also estimate λ, with the given standard ϵ of -4.96×10^{-5}, from this data using the formula;*

$$V^\circ = -\tfrac{1}{4F}(\lambda + \beta T + \epsilon P^\circ)$$

and taking a reading along the regression line to find the intercept. We found λ to be -1.16×10^5, -1.3×10^5 and -1.06×10^5, with a generally agreed upon value of -2.86×10^5.

Remarks 3.11. *Note on Negative Voltages*

When using negative voltages, $V - V^\circ(T) < 0$, it is necessary to reverse the sign of ϵ, or equivalently, reverse the sign in the Nernst equation, as we are then creating a positive voltage between the anode and cathode, which mimics the behaviour of the reaction at positive voltages between the cathode and anode, provided we reverse *the current, not the substance formed. This amounts to using the equation $I = -4F\frac{d\xi}{dt}$ at these voltages rather than $I = 4F\frac{d\xi}{dt}$, see* [13]*. We assume that voltage has the effect of always raising pressure above P°, otherwise, voltage would have a discontinuous effect on pressure. That is;*

$$V - V^\circ(T) = \tfrac{\epsilon(P-P^\circ)}{4F} \text{ if } V \leq V^\circ(T)$$

$$V - V^\circ(T) = \tfrac{-\epsilon(P-P^\circ)}{4F} \text{ if } V \geq V^\circ(T)$$

If we use the second equation to create pressure below P°, say $P = 0$;

$$V - V^\circ(T) = -\frac{\epsilon(0-P^\circ)}{4F}$$

$$= \frac{\epsilon P^\circ}{4F} < 0$$

then we have to use the first equation to lower the voltage $V - V^\circ(T)$ below $\frac{\epsilon P^\circ}{4F}$, and at that voltage;

$$\frac{\epsilon(P-P^\circ)}{4F} = \frac{\epsilon P^\circ}{4F}$$

$$P = 2P^\circ$$

so the pressure jumps from $P = 0$ to $P = 2P^\circ$ which is physically unreasonable. This continuity argument is also used to extend the scope of the equilibrium coefficient to the high pressures induced by voltage, when usual thermodynamic arguments no longer apply.

Remarks 3.12. *The Arrhenius equation is sometimes derived using kinetic theory, and allows for reactions to occur at constant temperature and pressure, which the above theory does not. However, there is a weakness in the kinetic theory argument, in that it assumes the temperature of the ensemble is not changed after a collision, when computing the number of collisions per second, proportional to the rate of reaction.*

We can also perform the above calculation for the reverse reaction of water electrolysis $2H_2O \to 2H_2 + O_2$. Then, we have that, using the same labels $\{n_1, n_2, n_3\}$ for hydrogen, oxygen and water respectively;

$$\frac{(n_1+2\xi)^2(n_2+\xi)}{(n_3-2\xi)^2(n+\xi)} = \frac{1}{Q}$$

to obtain that, using the above method, incorporating error terms into $\frac{1}{Q}$;

$$\xi'(0) = \frac{\nabla(\frac{1}{Q})n_3^2 n}{n_1^2+4n_1n_2+\frac{4}{Q}n_3n-\frac{1}{Q}n_3^2}$$

$$= -\frac{1}{Q^2}\frac{\nabla Q.\gamma' n_3^2 n}{n_1^2+4n_1n_2+\frac{4}{Q}n_3n-\frac{1}{Q}n_3^2}$$

$$= \frac{-\nabla Q.\gamma' n_3^2 n}{Q(Q(n_1^2+4n_1n_2)+4n_3n-n_3^2)}$$

$$\simeq \frac{-\nabla Q.\gamma' n_3^2 n}{Q(4n_3n-n_3^2)} \text{ (Newton's theorem } n_1^2 + 4n_1n_2 << 4n_3n - n_3^2)$$

$\simeq \frac{-\bigtriangledown Q \centerdot \gamma' n}{3Q}$, $(n_3 \simeq n)$

$\simeq \frac{-\bigtriangledown Q \centerdot \gamma' n x_1^2 x_2}{3}$, $(Q = \frac{x_3^2}{x_1^2 x_2}$, $x_3 \simeq 1)$

which is the negative of what we obtained in (FF) *above.*

Note that if $p(\xi) = Q(T, P)$, *with* $p(0) = Q(T_0, P_0)$, *then for a feasible path* γ*;*

$p'(\xi)|_0 \xi'(0) = \bigtriangledown(Q)(T_0, P_0) \centerdot \gamma'(0)$

so that, if $\frac{1}{p(-\xi)} = \frac{1}{Q(T,P)}$*;*

$\frac{-1}{p^2(-\xi)|_0}(-\xi'(0)) = -\frac{1}{Q^2(T_0,P_0)} \bigtriangledown (Q)(T_0, P_0) \centerdot \gamma'(0)$

$\xi'(0) = -\frac{p^2(0)}{Q^2(T_0,P_0)} \bigtriangledown (Q)(T_0, P_0) \centerdot \gamma'(0)$

$= - \bigtriangledown (Q)(T_0, P_0) \centerdot \gamma'(0)$

so the theoretical rate of the backward reaction is the negative of that of the forward reaction, as you would expect. This suggests that the approximations we are using are quite accurate. The kinetic theory would predict a larger rate of backward reaction, with $nx_1^2 x_2$ *in some way replaced by* $nx_3^2 \simeq n$*, which seems to be far too large, to the extent that it seems to deny the possibility of there ever being a fuel cell reaction. The idea that there can be a forward reaction and a backward reaction at the same time, to obtain the total reaction rate as the difference, violates Ockham's razor, as it simpler to suppose that there is no reaction at all rather than a forward reaction which cancels the backward reaction. In the above discussion, we used the rate law;*

$\xi'(t) = \frac{1}{3} \bigtriangledown (ln(Q))\gamma' n$

which when we reverse the reaction, replacing Q *by* $\frac{1}{Q}$ *becomes;*

$\xi'(t) = \frac{1}{3} \bigtriangledown (ln(\frac{1}{Q}))\gamma' n$

$= -\frac{1}{3} \bigtriangledown (ln(Q))\gamma' n$

which is again the negative of the forward reaction, as you would expect. When reversing the fuel cell reaction to electrolysis, it is not

necessary to reverse the voltage as well. One way of seeing this is to note that as we reverse the direction along a feasible path, keeping a positive voltage, the voltage itself may become negative relative to a fixed voltage or pressure at the turning point on the path. The induced reverse current effectively lowers the voltmeter reading. However, the Nernst equation only predicts positive voltages for the fuel cell reaction, as ϵ is negative, when $P > P^\circ$. When dealing with negative voltages, $V - V^\circ(T) < 0$, it is necessary to reverse the current, see Remark 3.11, while keeping the direction of reaction determined by the induced pressure change. Note also that $V^\circ = \frac{-1}{4F}\frac{\partial G}{\partial \xi}(T, P^\circ)$ does not *change sign, when moving from the fuel cell reaction to electrolysis presentation, as we are measuring the voltage between the fixed cathode in the fuel cell reaction to the fixed anode, which become the anode and cathode respectively in the electrolysis presentation, and clearly $\frac{\partial G}{\partial \xi}$ changes sign as well.*

with a predicted value of;

$$-\tfrac{1}{4F}(\lambda + \beta T + \epsilon P^\circ)$$

$$= -\tfrac{1}{4\times 96500}(-286000 + 829 \times 298 - 0.0000496 \times 101325)$$

$$= \tfrac{-1}{4\times 96500}(-286000 + 247042 - 5.02)$$

$$\simeq 0.1V$$

with the standard λ and $\beta = 829$ for the fuel cell reaction at 298K.

Lemma 3.13. *Energy formed over a temperature voltage loop: Voltage Hysteresis*

Let γ be a clockwise feasible loop in the temperature voltage plane. Then the total energy E liberated around the loop is given by;

$$E = \frac{n_0 e^{\frac{4F(V_0 - V^\circ(T_0))}{3RT_0}}}{3}\int_{S_\gamma} \tfrac{\epsilon}{RT^2}(-4FV - \lambda - \epsilon P^\circ)e^{\frac{-4F(V - V^\circ(T))}{3RT}} dS_\gamma$$

assuming $V > V^\circ(T)$ along the loop and S_γ is the interior of the loop. In particular;

$E > 0$ iff $V > \frac{\lambda + \epsilon P^\circ}{-4F}$ along the loop.

The equilibrium path defined between (T_1, V_0) *and* (T_2, V_0) $T_1 < T_2$, *with* $V_0 = \frac{\lambda+\epsilon P^\circ}{-4F}$ *is a minimum for the energy functional* E_γ, *restricted to paths satisfying* $V > V^\circ(T)$, *and reversing the direction, is a maximum. The energy functional evaluated at these paths is zero.*

Proof. Let S_γ be the region enclosed by the loop γ and Q' the equilibrium coefficient without the error term A. We have that, by Stokes' theorem;

$$E = \int_\gamma -(\lambda + \epsilon P + \beta T)\xi'$$

$$= \int_\gamma -(\lambda + \epsilon P + \beta T)\tfrac{1}{3} \bigtriangledown (ln(Q')) \centerdot \gamma' n_0 (\tfrac{Q'(T,P)}{Q'(T_0,P_0)})^{\frac{-1}{3}}$$

$$= -\tfrac{n_0 Q'(T_0,P_0)^{\frac{1}{3}}}{3} \int_\gamma (\lambda + \epsilon P + \beta T) Q'(T,P)^{\frac{-1}{3}} \bigtriangledown (ln(Q'))d\overline{\gamma}$$

$$= \tfrac{n_0 Q'(T_0,P_0)^{\frac{1}{3}}}{3} \int_{S_\gamma} \bigtriangledown \times [(\lambda + \epsilon P + \beta T) Q'(T,P)^{\frac{-1}{3}} \bigtriangledown (ln(Q'))]d\overline{S_\gamma}$$

$$= \tfrac{n_0 Q'(T_0,P_0)^{\frac{1}{3}}}{3} \int_{S_\gamma} \bigtriangledown [(\lambda + \epsilon P + \beta T) Q'(T,P)^{\frac{-1}{3}}] \times \bigtriangledown (ln(Q'))d\overline{S_\gamma}$$

$$= \tfrac{n_0 Q'(T_0,P_0)^{\frac{1}{3}}}{3} \int_{S_\gamma} [(\beta, \epsilon, 0) Q'(T,P)^{\frac{-1}{3}} + \bigtriangledown (Q'(T,P)^{\frac{-1}{3}})$$

$$(\lambda + \beta T + \epsilon P)] \times \bigtriangledown (ln(Q'))d\overline{S_\gamma}$$

$$= \tfrac{n_0 Q'(T_0,P_0)^{\frac{1}{3}}}{3} \int_{S_\gamma} [(0, 0, \tfrac{\beta\epsilon}{RT} + \tfrac{\epsilon^2(P-P^\circ)}{RT^2}) Q'(T,P)^{\frac{-1}{3}}] + [\bigtriangledown (Q'(T,P)^{\frac{-1}{3}})$$

$$(\lambda + \beta T + \epsilon P) \times \tfrac{\bigtriangledown (Q')}{Q'}]d\overline{S_\gamma}$$

$$= \tfrac{n_0 Q'(T_0,P_0)^{\frac{1}{3}}}{3} \int_{S_\gamma} [(0, 0, \tfrac{\beta\epsilon}{RT} + \tfrac{\epsilon^2(P-P^\circ)}{RT^2}) Q'(T,P)^{\frac{-1}{3}}]$$

$$-[Q'(T,P)^{\frac{-4}{3}} (\lambda + \beta T + \epsilon P) \bigtriangledown (Q') \times \tfrac{\bigtriangledown (Q')}{Q'}]d\overline{S_\gamma}$$

$$= \tfrac{n_0 Q'(T_0,P_0)^{\frac{1}{3}}}{3} \int_{S_\gamma} [(0, 0, \tfrac{\beta\epsilon}{RT} + \tfrac{\epsilon^2(P-P^\circ)}{RT^2}) Q'(T,P)^{\frac{-1}{3}}]d\overline{S_\gamma}$$

$$= \tfrac{n_0 Q'(T_0,P_0)^{\frac{1}{3}}}{3} \int_{S_\gamma} (\tfrac{\beta\epsilon}{RT} + \tfrac{\epsilon^2(P-P^\circ)}{RT^2}) Q'(T,P)^{\frac{-1}{3}} dS_\gamma$$

$$= \tfrac{n_0 Q'(T_0,P_0)^{\frac{1}{3}}}{3} \int_{S_\gamma} (\tfrac{\beta\epsilon}{RT} - \tfrac{4F\epsilon(V-V^\circ(T))}{RT^2}) Q'(T,P)^{\frac{-1}{3}} dS_\gamma \ (V > V^\circ(T))$$

$$= \tfrac{n_0 Q'(T_0,P_0)^{\frac{1}{3}}}{3} \int_{S_\gamma} \tfrac{\epsilon}{RT^2} (\beta T - 4F(V - V^\circ(T))) Q'(T,P)^{\frac{-1}{3}} dS_\gamma$$

$= \frac{n_0 Q'(T_0,P_0)^{\frac{1}{3}}}{3} \int_{S_\gamma} \frac{\epsilon}{RT^2}(\beta T - 4F(V - (\frac{-1}{4F})(\lambda + \beta T + \epsilon P^\circ)))Q'(T,P)^{\frac{-1}{3}} dS_\gamma$

$= \frac{n_0 Q'(T_0,P_0)^{\frac{1}{3}}}{3} \int_{S_\gamma} \frac{\epsilon}{RT^2}(\beta T - 4FV - (\lambda + \beta T + \epsilon P^\circ))Q'(T,P)^{\frac{-1}{3}} dS_\gamma$

$= \frac{n_0 Q'(T_0,P_0)^{\frac{1}{3}}}{3} \int_{S_\gamma} \frac{\epsilon}{RT^2}(-4FV - \lambda - \epsilon P^\circ)Q'(T,P)^{\frac{-1}{3}} dS_\gamma$

We have that, using the equations;

$Q'(T,P) = e^{\frac{\epsilon(P-P^\circ)}{RT}}$

$V - V^\circ(T) = -\frac{\epsilon}{4F}(P - P^\circ)$

$Q'(T,P)^{\frac{-1}{3}} = e^{\frac{-4F(V-V^\circ(T))}{3RT}}$

$Q'(T_0,P_0)^{\frac{1}{3}} = e^{\frac{4F(V_0-V^\circ(T_0))}{3RT_0}}$

so that;

$E = \frac{n_0 e^{\frac{4F(V_0-V^\circ(T_0))}{3RT_0}}}{3} \int_{S_\gamma} \frac{\epsilon}{RT^2}(-4FV - \lambda - \epsilon P^\circ)e^{\frac{-4F(V-V^\circ(T))}{3RT}} dS_\gamma$

The second claim follows, noting that $\epsilon < 0$, so that;

$\frac{\epsilon}{RT^2}(-4FV - \lambda - \epsilon P^\circ) > 0$

iff $(-4FV - \lambda - \epsilon P^\circ) < 0$

iff $V > \frac{\lambda + \epsilon P^\circ}{-4F}$

Using the above calculation, we have that;

$\frac{\beta\epsilon}{RT} - \frac{4F\epsilon(V - V^\circ(T))}{RT^2} = 0$

iff $\beta T = 4F(V - V^\circ(T))$

iff $V = \frac{\lambda + \epsilon P^\circ}{-4F}$

iff $\beta T = -\epsilon(P - P^\circ)$

iff $Q'(T,P) = e^{\frac{\epsilon(P-P^\circ)}{RT}} = e^{\frac{-\beta}{R}}$

so that Q is constant along the equilibrium line $V = \frac{\lambda+\epsilon P^\circ}{-4F}$ and no substance ξ is formed, for a feasible path $\gamma_1 \subset (V = \frac{\lambda+\epsilon P^\circ}{-4F})$, between (T_1, V_0) and (T_2, V_0), with $T_1 < T_2$, $V_0 = \frac{\lambda+\epsilon P^\circ}{-4F}$. In particular $E_{\gamma_1}(T_2, V_0) = 0$.

Note that $V = V^\circ(T)$ intersects the line $V = \frac{\lambda+\epsilon P^\circ}{-4F}$ at $T = 0$, and lies beneath it in the temperature voltage plane, with $T > 0$, so that $V > V^\circ(T)$ is satisfied for γ_1. If γ_2 is a feasible path between between (T_1, V_0) and (T_2, V_0), $V - V^\circ(T) > 0$, which does not intersect γ_1 except at (T_1, V_0) and (T_2, V_0), then if $\gamma_2^{-1} \circ \gamma_1$ forms a clockwise feasible loop, with $V > V^\circ(T)$ again, we have that $E = E_{\gamma_1} - E_{\gamma_2} < 0$, as $-4FV - \lambda - \epsilon P^\circ < 0$ on the interior of the loop. If $\gamma_2^{-1} \circ \gamma_1$ forms an anticlockwise feasible loop, so that $V > V^\circ(T)$ again automatically, we have that $E = E_{\gamma_1} - E_{\gamma_2} < 0$ again, as $-4FV - \lambda - \epsilon P^\circ > 0$ on the interior of the loop, but there is a change in sign due to the application of Stokes' Theorem. We conclude that for all such paths $0 = E_{\gamma_1} < E_{\gamma_2}$. Reversing the direction of such paths, we obtain $E_{\gamma_2} < 0$. The result can be generalised to any path from (T_1, V_0) to (T_2, V_0), by dividing the loop $\gamma_2^{-1} \circ \gamma_1$ into subloops formed by the intersections with γ_1, assuming the condition $V > V^\circ(T)$ along the path.

□

Remarks 3.14. *The energy of voltage hysteresis is liberated in the heat of the reaction along the loop. It is not clear this violates the second law of thermodynamics, as we are not extracting heat perfectly when varying the voltage in a hysteresis loop. An alternative theory, which does not contradict conservation of energy, is that ambient light provides or absorbs energy during the reaction, by the photoelectric effect. This idea overlaps with ideas in biology when we consider the reaction cycle for photosynthesis in plants. It is an appealing idea that voltage hysteresis drives the production of plasmas in stars, leading to the stable production of power by nuclear fusion. Some work in this direction is carried out in* [13]. *The phenomenon is converse to the contradictory machine proposed if substance is formed in a loop, where heat can be extracted perfectly to drive a motor. The theory can be tested with an electrolyzer and fuel cell which are in thermal equilibrium, such that the hydrogen output from the electrolyser is connected to the hydrogen input from the fuel cell, and there is a the same amount of water in both containers, see Lemma 3.16.*

We should decrease the temperature, while increasing and then lowering the voltage above the critical value of $\frac{\lambda+\epsilon P^\circ}{-4F}$ *to liberate energy.*

The direction of the reaction is determined by the sign of;

$$\bigtriangledown(ln(Q)) \cdot \gamma'$$

$$= -\frac{\epsilon(P-P^\circ)}{RT^2}T' + \frac{\epsilon}{RT}P'$$

so that if $T' < 0$, $P' > 0$, $\bigtriangledown(ln(Q)) \cdot \gamma' < 0$, *and, as* $\epsilon < 0$, *hydrogen is liberated along the path, as we decrease the temperature and increase the voltage. Beyond a critical point on the path, as we lower the voltage, the hydrogen will then be consumed in the fuel cell, as* $V = \frac{\lambda+\epsilon P^\circ}{-4F}$ *is an equilibrium line. The energy liberated at the fuel cell terminal will be greater than that consumed by electrolysis. As noted above, the voltage across the fuel cell must be the same as the electrolyser, because the pressures are the same.*

Definition 3.15. *We say that two electrolytic cells for the production of hydrogen and oxygen from water are in thermal equilibrium if they are at the same temperature, and in hydrogen equilibrium if the partial pressure* $P(H_2)$ *is the same for both cells. By Raoult's law, assuming* k_{H_2} *is constant, this implies the concentration of hydrogen is the same for both cells. The example we have in mind is an electrolyser and a fuel cell, such that the output of hydrogen from the electrolyser is connected to the input of the fuel cell.*

Lemma 3.16. *If two electrolytic cells are in thermal equilibrium and hydrogen equilibrium, with initial molar amounts* $\{n_0^1, n_0^2\}$ *at* (T, P°), *then the ratio of substance formed is given by;*

$$\frac{\xi_2}{\xi_1} = \frac{n_0^2}{n_0^1}$$

Moreover, the cells are at the same potential. If $n_0^1 = n_0^2$, *then the current through the cells is the same, and in general;*

$$\frac{I_2}{I_1} = \frac{n_0^2}{n_0^1}$$

Proof. We have that, for the first cell;

$$x^1_{H_2}(T, P) = \frac{n^1_{H_2}}{n^1} = \frac{n^1_{H_2,0}-2\xi_1}{n_0^1-\xi_1}$$

where ξ_1 is the substance formed. Rearranging, we obtain that;

$$\xi_1 = \frac{n^1_{H_2,0} - n^1_0 x^1_{H_2}}{2 - x^1_{H_2}}$$

$$= \frac{n^1_0[\frac{n^1_{H_2,0}}{n^1_0} - x^1_{H_2}]}{2 - x^1_{H_2}}$$

Similarly, as the two cells are in hydrogen equilibrium;

$$\xi_2 = \frac{n^2_{H_2,0} - n^2_0 x^2_{H_2}}{2 - x^2_{H_2}}$$

$$= \frac{n^2_{H_2,0} - n^2_0 x^1_{H_2}}{2 - x^1_{H_2}}$$

$$= \frac{n^2_0[\frac{n^2_{H_2,0}}{n^2_0} - x^1_{H_2}]}{2 - x^1_{H_2}}$$

$$= \frac{n^2_0[\frac{n^1_{H_2,0}}{n^1_0} - x^1_{H_2}]}{2 - x^1_{H_2}}$$

$$= \frac{n^2_0 \xi_1}{n^1_0}$$

which is the first claim. For the second claim, we claim that the pressure of water from electrolysis is the same in both cells. We have for the first cell, that;

$$\xi_1(T, P) = n^1_0(1 - (\frac{q(T,P)}{q_0})^{\frac{-1}{3}})$$

and applying the first result, using thermal equilibrium;

$$\xi_2(T, P') = \frac{n^2_0 \xi_1}{n^1_0}$$

$$= n^2_0(1 - (\frac{q(T,P)}{q_0})^{\frac{-1}{3}})$$

$$= n^2_0(1 - (\frac{q(T,P')}{q_0})^{\frac{-1}{3}})$$

so that $q(T, P) = q(T, P')$ and, therefore, $P = P'$. Using the Nernst equation;

$$V_1(T, P) - V^\circ_1(T) = \frac{RT}{-4F} ln(q)(T, P)$$

$$= \frac{RT}{-4F} ln(q)(T, P')$$

$= V_2(T, P') - V_2^\circ(T)$

we obtain $V_1 = V_2$, so the potentials are the same. Using the fact that;

$I_2(T, P) = -4F\frac{d\xi_2}{dt}$

$= -4F\frac{n_0^2}{n_0^1}\frac{d\xi_1}{dt}$

$= \frac{n_0^2}{n_0^1} I_1(T, P)$

we obtain the last results on the currents.

□

When connecting an electrolyser to a fuel cell, it is necessary to obtain a high partial pressure of hydrogen to force a reaction in the fuel cell. This is theoretically predicted at high voltages by the following result.

Lemma 3.17. *Formula for partial pressure during electrolysis*

Assuming that $P(H_2) \simeq P(O_2)$ during electrolysis, and the Henry's law coefficients $\{k_{H_2}, k_{O_2}\}$ are independent of pressure, then we have that;

$P_{H_2} \simeq P_{O_2} \simeq P^\circ e^{\frac{4F(V-V^\circ)}{3RT}}$ $(V > V^\circ)$

Proof. We have that;

$x_{H_2}(T, P^\circ) = \frac{P^\circ}{k_{H_2}}$

for the constant k_{H_2} appearing in Henry's law, assuming that $P_{H_2} = P^\circ$ at P° the pressure of water. Moreover;

$\mu_{H_2}(T, P) = \mu_{H_2}^\circ + RTln(x_{H_2}) + RTln(\frac{k_{H_2}}{P^\circ})$

so that;

$x_{H_2}(T, P) = e^{\frac{\mu_{H_2} - \mu_{H_2}^\circ}{RT}}(\frac{P^\circ}{k_{H_2}})$

and by Henry's law;

$$P_{H_2} = k_{H_2} x_{H_2} = P^\circ e^{\frac{\mu_{H_2} - \mu^\circ_{H_2}}{RT}} \ (A)$$

The same calculation applies to O_2.

For the solvent H_2O, we have that;

$$\mu_{H_2O} = \mu^\circ_{H_2O} + RTln(\frac{x_{H_2O}}{x^\circ_{H_2O}})$$

and, for a dilute solution;

$$\frac{x_{H_2O}}{x^\circ_{H_2O}} \simeq 1$$

so that;

$$e^{\frac{\nu_{H_2O}(\mu_{H_2O} - \mu^\circ_{H_2O})}{RT}} \simeq 1^{\nu_{H_2O}} \simeq 1$$

$$P^\circ e^{\frac{\nu_{H_2O}(\mu_{H_2O} - \mu^\circ_{H_2O})}{RT}} \simeq P^\circ \ (B)$$

Combining $(A), (B)$, we obtain that;

$$P_{H_2}^{\nu_{H_2}} P_{O_2}^{\nu_{O_2}} P^\circ \simeq (P^\circ)^{\nu_{H_2} + \nu_{O_2} + 1} e^{\frac{\sum_{i=1}^3 \nu_i(\mu_i - \mu_i^\circ)}{RT}}$$

$$= (P^\circ)^{\nu_{H_2} + \nu_{O_2} + 1} e^{\frac{\frac{\partial G}{\partial \xi}(T,P) - \frac{\partial G}{\partial \xi}(T,P^\circ)}{RT}}$$

$$= (P^\circ)^{\nu_{H_2} + \nu_{O_2} + 1} Q_0(T,P)$$

$$= (P^\circ)^{\nu_{H_2} + \nu_{O_2} + 1} e^{\frac{\epsilon(P - P^\circ)}{RT}} \ (C)$$

Assuming that $P_{H_2} \simeq P_{O_2}$, and with $\nu_{H_2} = -2$, $\nu_{O_2} = -1$ for the fuel cell reaction, we obtain, from (C);

$$P_{H_2} \simeq P^\circ e^{\frac{-\epsilon(P - P^\circ)}{3RT}}$$

By the Nernst equation, with $V > V^\circ$;

$$V - V^\circ = -\frac{RTln(Q_0)}{4F}$$

$= -\frac{\epsilon(P-P^\circ)}{4F}$

so that;

$P_{H_2} \simeq P^\circ e^{\frac{4F(V-V^\circ)}{3RT}}$

as required.

The last claim is clear by symmetry.

□

Lemma 3.18. *Assuming the coefficients in Henry's law are independent of pressure, then we have that;*

$\frac{P_{H_2}}{P_{O_2}} = 4$

for the fuel cell reaction, with;

$P_{H_2,\circ} = 4P^\circ$

$P_{O_2,\circ} = P^\circ$

Proof. Assume that $P_{H_2,\circ} = sP^\circ$, $P_{O_2,\circ} = tP^\circ$, then;

$\mu_{H_2}^{\circ,(g)} = \mu_{H_2}^\circ - RTln(s)$

$\mu_{O_2}^{\circ,(g)} = \mu_{O_2}^\circ - RTln(t)$

$\mu_{H_2} = \mu_{H_2}^\circ + RTln(x_{H_2}) + RTln(\frac{k_{H_2}}{sP^\circ})$

$\mu_{O_2} = \mu_{O_2}^\circ + RTln(x_{O_2}) + RTln(\frac{k_{H_2}}{tP^\circ})$

$x_{H_2}^\circ = \frac{sP^\circ}{k_{H_2}^\circ}$

$x_{O_2}^\circ = \frac{tP^\circ}{k_{O_2}^\circ}$

Then, using Henry's law;

$\frac{P_{H_2}}{P_{O_2}}(T,P) = \frac{k_{H_2}}{k_{O_2}}\frac{x_{H_2}}{x_{O_2}}$

$= \frac{k_{H_2}}{k_{O_2}} \frac{n_{H_2}}{n_{O_2}}$

$= \frac{k_{H_2}}{k_{O_2}} \frac{n^\circ_{H_2} - 2\xi}{n^\circ_{O_2} - \xi}$

We have that;

$\frac{n^\circ_{O_2}}{n^\circ_{H_2}} = \frac{x^\circ_{O_2}}{x^\circ_{H_2}}$

$= \frac{\frac{tP^\circ}{k^\circ_{O_2}}}{\frac{sP^\circ}{k^\circ_{H_2}}}$

$= \frac{t}{s} \frac{k^\circ_{H_2}}{k^\circ_{O_2}}$

so that, as $k_{H_2} = k^\circ_{H_2}$ and $k_{O_2} = k^\circ_{O_2}$;

$\frac{P_{H_2}}{P_{O_2}}(T, P) = \frac{k_{H_2} n^\circ_{H_2} - 2k_{H_2}\xi}{k_{O_2}(\frac{t}{s}\frac{k^\circ_{H_2}}{k^\circ_{O_2}} n^\circ_{H_2}) - k_{O_2}\xi}$

$= \frac{k_{H_2} n^\circ_{H_2} - 2k_{H_2}\xi}{\frac{t}{s} k_{H_2} n^\circ_{H_2} - k_{O_2}\xi}$

From a table, we have that, at room temperature $T_0 = 296K$;

$\frac{k_{O_2}}{k_{H_2}} \simeq \frac{1}{2}$

Using the van't Hoff equation, with the temperature dependence $e^{-\frac{\Delta_{sol}}{R}(\frac{1}{T} - \frac{1}{T_\circ})}$ in the Henry's law constants, for oxygen and hydrogen dissolved in water, we can assume that;

$\frac{k_{O_2}}{k_{H_2}} \simeq \frac{1}{2} e^{[\frac{(\Delta_{sol,H_2} - \Delta_{sol,O_2})}{R}](\frac{1}{T} - \frac{1}{T_0})}$

$\simeq \frac{1}{2} e^{1200(\frac{1}{T} - \frac{1}{T_0})}$

$\simeq \frac{1}{2} e^{4(\frac{T_0 - T}{T})}$

$= \frac{1}{2} e^{-4} e^{4\frac{T_0}{T}}$

$\simeq \frac{1}{2}$

as the temperature dependence $e^{-4} e^{\frac{4T_0}{T}}$ is close to unity within the usual temperature range, so that, with $\frac{t}{s} = \frac{1}{4}$;

$$\frac{P_{H_2}}{P_{O_2}}(T,P)$$
$$= \frac{k_{H_2}n^{\circ}_{H_2} - 2k_{H_2}\xi}{\frac{1}{4}k_{H_2}n^{\circ}_{H_2} - \frac{k_{H_2}}{2}\xi}$$
$$= 4$$

□

Remarks 3.19. *Observe that if you want a more accurate result, we* can *vary* $\frac{t}{s} = \frac{1}{4}e^{-4}e^{4\frac{T_0}{T}}$ *with temperature, using a piston controlled by temperature. We then get a temperature dependence* $4e^4e^{-4\frac{T_0}{T}}$ *in the ratio* $\frac{P_{H_2}}{P_{O_2}}(T,P)$ *and a further temperature dependence in the partial pressures given in Lemma 3.20.*

Lemma 3.20. *Assuming that;*

$$P_{H_2,\circ} = 4P^{\circ}$$

$$P_{O_2,\circ} = P^{\circ}$$

then we have, with the same assumptions as in Lemma 3.18, that;

$$P_{H_2} \simeq 4P^{\circ}e^{\frac{4F(V-V^{\circ})}{3RT}} \ (V > V^{\circ})$$

$$P_{O_2} \simeq P^{\circ}e^{\frac{4F(V-V^{\circ})}{3RT}} \ (V > V^{\circ})$$

Proof. By Lemma 3.18, we have that $\frac{P_{H_2}}{P_{O_2}} = 4$, $(*)$. The rest of the claim is clear following through the proof of Lemma 3.17, noting that;

$$P_{H_2} = 4P^{\circ}e^{\frac{\mu_{H_2}-\mu^{\circ}_{H_2}}{RT}}$$

$$P_{O_2} = P^{\circ}e^{\frac{\mu_{O_2}-\mu^{\circ}_{O_2}}{RT}} \ (A')$$

(B) is the same, and then;

$$P_{H_2}^{\nu_{H_2}}P_{O_2}^{\nu_{O_2}}P^{\circ} \simeq 4^{\nu_{H_2}}(P^{\circ})^{\nu_{H_2}+\nu_{O_2}+1}e^{\frac{\epsilon(P-P^{\circ})}{RT}} \ (C)'$$

so that;

$P_{H_2}^{\nu_{H_2}} \frac{P_{H_2}}{4}^{\nu_{O_2}} P^\circ \simeq 4^{\nu_{H_2}} (P^\circ)^{\nu_{H_2}+\nu_{O_2}+1} e^{\frac{\epsilon(P-P^\circ)}{RT}}$

and;

$P_{H_2}^{\nu_{H_2}+\nu_{O_2}} P^\circ \simeq 4^{\nu_{H_2}+\nu_{O_2}} (P^\circ)^{\nu_{H_2}+\nu_{O_2}+1} e^{\frac{\epsilon(P-P^\circ)}{RT}}$

so that;

$P_{H_2} \simeq 4P^\circ e^{\frac{-\epsilon(P-P^\circ)}{3RT}}$ $(V > V^\circ)$

and the rest of the proof is the same, to get;

$P_{H_2} \simeq 4P^\circ e^{\frac{4F(V-V^\circ)}{3RT}}$ $(V > V^\circ)$

$P_{O_2} \simeq P^\circ e^{\frac{4F(V-V^\circ)}{3RT}}$ $(V > V^\circ)$

by symmetry.

□

Lemma 3.21. *Energy per mole over a temperature voltage path Let γ be a path between (T_0, P_0) and (T, P) such that a non zero amount of substance ξ is formed along γ. We have that, letting q be the equilibrium coefficient without the error term A;*

$E = \int_\gamma -(\lambda + \epsilon P + \beta T) \frac{1}{3} \bigtriangledown (ln(q)) \centerdot \gamma' n_0 (\frac{q(T,P)}{q(T_0,P_0)})^{\frac{-1}{3}}$

$\xi = n_0 (1 - (\frac{q}{q_0})^{\frac{-1}{3}})$

$\frac{E}{\xi} = \frac{1}{q_0^{\frac{-1}{3}} - q^{\frac{-1}{3}}} \int_\gamma (\lambda + \epsilon P + \beta T) \bigtriangledown (q^{\frac{-1}{3}}) \centerdot \gamma'$

Assume that $V > V^\circ(T)$ along the path γ, then γ is not *a local minimum or maximum for the functional $\frac{E}{\xi}$.*

Proof. The first two claims are a recap of what has already been proved;

$E = \int_\gamma -(\lambda + \epsilon P + \beta T) \xi'$

$= \int_\gamma -(\lambda + \epsilon P + \beta T) \frac{1}{3} \bigtriangledown (ln(q)) \centerdot \gamma' n_0 (\frac{q(T,P)}{q(T_0,P_0)})^{\frac{-1}{3}}$

$\xi = n_0(1 - (\frac{q}{q_0})^{\frac{-1}{3}})$

The third claim is a simple rearrangement;

$$\frac{E}{\xi} = -\frac{1}{3}\frac{q_0^{\frac{1}{3}}}{1-(\frac{q}{q_0})^{\frac{-1}{3}}}\int_\gamma(\lambda + \epsilon P + \beta T) \bigtriangledown (ln(q)) \centerdot \gamma' q^{\frac{-1}{3}}$$
$$= -\frac{1}{3}\frac{1}{q_0^{\frac{-1}{3}} - q^{\frac{-1}{3}}}\int_\gamma(\lambda + \epsilon P + \beta T) \bigtriangledown (q) \centerdot \gamma' q^{\frac{-4}{3}}$$
$$= \frac{1}{q_0^{\frac{-1}{3}} - q^{\frac{-1}{3}}}\int_\gamma(\lambda + \epsilon P + \beta T) \bigtriangledown (q^{\frac{-1}{3}}) \centerdot \gamma'$$

For the final claim, we can assume, without loss of generality that either (T_0, P_0) or (T, P) does *not* lie on the equilibrium line defined by;

$V = \frac{\lambda + \epsilon P^\circ}{-4F}$

otherwise, as no substance ξ is formed in a loop, $\xi = 0$, contradicting the hypothesis.

Suppose that (T_0, P_0) lies above the equilibrium line $\beta T = -\epsilon(P - P^\circ)$, see the calculation in Lemma 3.13, and choose a small loop γ_2 centred at (T_0, P_0), which does not intersect this line. As we saw in Lemma 3.13, $(-4FV - \lambda - \epsilon P^\circ) < 0$ on the interior of the loop, so by choosing γ_2 to be clockwise or anticlockwise, we have that the energy E_{γ_2} liberated along the loop is less than zero or greater than zero respectively, with no substance ξ_2 formed. In either case, considering the path $\gamma \circ \gamma_2$ from (T_0, P_0) to (T, P), we have that the substance ξ formed is the same $\xi_2 + \xi = \xi$, while the energy liberated is $E_{\gamma\circ\gamma_2} = E_{\gamma_2} + E_\gamma < E_\gamma$ or $E_{\gamma\circ\gamma_2} = E_{\gamma_2} + E_\gamma > E_\gamma$. The other cases are similar, composing with end loops and reversing the direction of the loop if necessary. This proves that γ is *not* a local minimum or maximum for the functional $\frac{E}{\xi}$.

□

Lemma 3.22. *Energy over a temperature voltage path*

For $V > V^\circ(T)$, the only extremal paths in the temperature voltage plane are given by those in Lemma 3.13, that is paths whose range lie within the equilibrium line $V = \frac{\lambda + \epsilon P^\circ}{-4F}$.

Proof. We have that;

$E = \int_\gamma -(\lambda + \epsilon P + \beta T)\frac{1}{3} \bigtriangledown (ln(q)) \centerdot \gamma' n_0 (\frac{q(T,P)}{q(T_0,P_0)})^{\frac{-1}{3}}$

$= -\frac{n_0}{3q_0^{\frac{-1}{3}}} \int_\gamma (\lambda + \epsilon P + \beta T) q^{\frac{-4}{3}} \bigtriangledown (q) \centerdot \gamma'$

$= -\frac{n_0}{3q_0^{\frac{-1}{3}}} \int_\gamma (\lambda + \epsilon P + \beta T)(q_T T' + q_P P') q^{\frac{-4}{3}}$

and the Euler Lagrange equation for $\int_\gamma (\lambda+\epsilon P+\beta T)(q_T T'+q_P P')q^{\frac{-4}{3}}$ are given by;

$(i).\ \frac{\partial[(\lambda+\epsilon P+\beta T)(q_T T'+q_P P')q^{\frac{-4}{3}}]}{\partial T} - \frac{d}{dt}(\frac{\partial[(\lambda+\epsilon P+\beta T)(q_T T'+q_P P')q^{\frac{-4}{3}}]}{\partial T'}) = 0$

iff

$\beta(q_T T' + q_P P')q^{\frac{-4}{3}} + (\lambda + \epsilon P + \beta T)(q_{TT} T' + q_{TP} P')q^{\frac{-4}{3}} + (\lambda + \epsilon P$

$+\beta T)(q_T T' + q_P P')(\frac{-4}{3} q^{\frac{-7}{3}} q_T) - \frac{d}{dt}(((\lambda + \epsilon P + \beta T))q_T q^{\frac{-4}{3}}) = 0$

iff

$\beta(q_T T' + q_P P')q^{\frac{-4}{3}} + (\lambda + \epsilon P + \beta T)(q_{TT} T' + q_{TP} P')q^{\frac{-4}{3}} + (\lambda + \epsilon P$

$+\beta T)(q_T T' + q_P P')(\frac{-4}{3} q^{\frac{-7}{3}} q_T) - (\epsilon P' + \beta T')q_T q^{\frac{-4}{3}} - (\lambda + \epsilon P + \beta T)$

$(q_{TT} T' + q_{TP} P')q^{\frac{-4}{3}} - (\lambda + \epsilon P + \beta T)(q_T T' + q_P P')(\frac{-4}{3} q_T q^{\frac{-7}{3}}) = 0$

iff

$\beta(q_T T' + q_P P')q^{\frac{-4}{3}} - (\epsilon P' + \beta T')q_T q^{\frac{-4}{3}} = 0$

iff

$\beta(q_T T' + q_P P') - (\epsilon P' + \beta T')q_T = 0$

iff

$\beta q_P P' = \epsilon q_T P'$

iff $P' = 0$ or $\frac{q_P}{q_T} = \frac{\epsilon}{\beta}$

$(ii).\ \frac{\partial[(\lambda+\epsilon P+\beta T)(q_T T'+q_P P')q^{\frac{-4}{3}}]}{\partial P} - \frac{d}{dt}(\frac{\partial[(\lambda+\epsilon P+\beta T)(q_T T'+q_P P')q^{\frac{-4}{3}}]}{\partial P'}) = 0$

iff

$$\epsilon(q_T T' + q_P P')q^{\frac{-4}{3}} + (\lambda + \epsilon P + \beta T)(q_{TP} T' + q_{PP} P')q^{\frac{-4}{3}} + (\lambda + \epsilon P$$

$$+\beta T)(q_T T' + q_P P')(\tfrac{-4}{3} q^{\frac{-7}{3}} q_P) - \tfrac{d}{dt}(((\lambda + \epsilon P + \beta T))q_P q^{\frac{-4}{3}}) = 0$$

iff

$$\epsilon(q_T T' + q_P P')q^{\frac{-4}{3}} + (\lambda + \epsilon P + \beta T)(q_{TP} T' + q_{PP} P')q^{\frac{-4}{3}} + (\lambda + \epsilon P$$

$$+\beta T)(q_T T' + q_P P')(\tfrac{-4}{3} q^{\frac{-7}{3}} q_P) - (\epsilon P' + \beta T')q_P q^{\frac{-4}{3}} - (\lambda + \epsilon P + \beta T)$$

$$(q_{TP} T' + q_{PP} P')q^{\frac{-4}{3}} - (\lambda + \epsilon P + \beta T)(q_T T' + q_P P')(\tfrac{-4}{3} q_P q^{\frac{-7}{3}}) = 0$$

iff

$$\epsilon(q_T T' + q_P P')q^{\frac{-4}{3}} - (\epsilon P' + \beta T')q_P q^{\frac{-4}{3}} = 0$$

iff

$$\epsilon(q_T T' + q_P P') - (\epsilon P' + \beta T')q_P = 0$$

iff

$$\beta q_P T' = \epsilon q_T T'$$

iff $T' = 0$ or $\frac{q_P}{q_T} = \frac{\epsilon}{\beta}$

The result tells us that, to be an energy extremal, the range of the path γ must be a subset of the equilibrium line defined by;

$$\frac{q_P}{q_T} = \frac{\epsilon}{\beta}$$

iff $\frac{\frac{\epsilon q}{RT}}{-\frac{\epsilon(P-P^\circ)q}{RT^2}} = \frac{\epsilon}{\beta}$

iff $\beta T = -\epsilon(P - P^\circ)$ (C)

so that, with the Nernst equation, assuming $V > V^\circ(T)$;

$$V - V^\circ(T) = -\tfrac{\epsilon}{4F}(P - P^\circ)$$

iff $\beta T = 4F(V - V^{\circ}(T))$

iff $V = \frac{\lambda + \epsilon P^{\circ}}{-4F}$

□

4. Electrochemistry with error terms and ideal solution

We consider the reaction $H_2(g) + 2AgCl(s) + 2e^-(R) \rightarrow 2HCl + 2Ag(s) + 2e^-(L)$, for the standard cell, even though the uncharged species probably don't form an ideal solution. The reader can easily reformulate the results in the context of an ideal solution, by just changing the electron count, see Section 9.

Lemma 4.1. *The Nernst Equation for the Standard Cell*

At electrical chemical equilibrium (T, P) *and* (T, P°)*;*

$(E - E^{\circ})(T, P) = -\frac{RTln(Q(T,P))}{2F} - \frac{\epsilon(T,P)}{2F}$

Proof. For c substances, with c' the number of the charged species,using Definition 2.1, we have that the electrostatic potential energy;

$U_{el} = \sum_{i=1}^{c'} \phi(\overline{x}_i) q_i$, where $q_i = N_i e z_i = N_A n_i e z_i$

where $\{\overline{x}_i : 1 \leq i \leq c'\}$ are the positions of the charged species, N_i is the number of particles at $\overline{x}_i$.

We have that;

$U = U_{chem} + U_{el}$, so that;

$G(T, P, n_1, \ldots, n_c) = U + PV - TS$

$= U_{chem} + U_{el} + PV - TS$

$= U_{el} + G_{chem}$

$= \sum_{j=1}^{c} \phi(\overline{x}_j) q_j + G_{chem}$

$= \sum_{j=1}^{c} \phi(\overline{x}_j) N_A n_j e z_j + G_{chem}$

so that;

$\mu_i = (\frac{\partial G}{\partial n_i})_{T,P}$

$= (\frac{\partial(\sum_{j=1}^{c} \phi(\overline{x}_j) N_A n_j e z_j + G_{chem})}{\partial n_i})_{T,P}$

$= \mu_{i,chem},\ (c' + 1 \leq i \leq c)$

$= \mu_{i,chem} + \frac{\partial(\phi(\overline{x}_i) N_A n_i e z_i)}{\partial n_i},\ (1 \leq i \leq c')$

$= \mu_{i,chem} + \phi(\overline{x}_i) N_A e z_i$

$= \mu_{i,chem} + \phi(\overline{x}_i) F z_i,\ (*)$

We consider the standard cell reaction $H_2(g) + 2AgCl(s) + 2e^-(R) \rightarrow 2HCl + 2Ag(s) + 2e^-(L)$. At electrical chemical equilibrium, similarly to Lemma 2.10, generalised to a collection involving charged species, using $(*)$, we have that;

$(\frac{\partial G}{\partial \xi})_{T,P} = \sum_{i=1}^{c} \nu_i \mu_i$

$= 2\mu(HCl) + 2\mu(Ag) - \mu(H_2) - 2\mu(AgCl) + 2\mu(e^-(L)) - 2\mu(e^-(R))$

$= (\frac{\partial G_{chem'}}{\partial \xi})_{T,P} + 2\mu(e^-(L)) - 2\mu(e^-(R))$

$= (\frac{\partial G_{chem'}}{\partial \xi})_{T,P} + ((2\mu_{chem}(e^-(L)) - 2F\phi(L)) - (2\mu_{chem}(e^-(L)) - 2F\phi(R)))$

$= (\frac{\partial G_{chem'}}{\partial \xi})_{T,P} + 2F(\phi(R) - \phi(L))$

$= (\frac{\partial G_{chem'}}{\partial \xi})_{T,P} + 2EF = 0\ (\dagger)$

where $G_{chem'}$ is the Gibbs energy restricted to the uncharged species. By Lemmas 3.2 and 3.3, we have that;

$(\frac{\partial G_{chem'}}{\partial \xi})_{T,P^\circ} = \sum_{i=c'+1}^{c} \nu_i \mu_i^\circ$

$= (\Delta G^\circ_{chem'} + RTln(Q_{chem'}(T, P^\circ)) + \epsilon(T, P^\circ))$

$= (\Delta G^\circ_{chem'} - \epsilon(P^\circ)) + \epsilon(T, P^\circ))$

$= \Delta G^{\circ}_{chem'}$, $(\dagger\dagger)$

From $(\dagger), (\dagger\dagger)$, we obtain;

$2E^{\circ}F = -(\frac{\partial G_{chem'}}{\partial \xi})_{T,P^{\circ}}$

$= -\Delta G^{\circ}_{chem'}$ $(\dagger\dagger\dagger)$

Similarly, we have that;

$(\frac{\partial G_{chem'}}{\partial \xi})_{T,P} = \sum_{i=c'+1}^{c} \nu_i \mu_i$

$= (\Delta G^{\circ}_{chem'} + RTln(Q_{chem'}(T,P)) + \epsilon(T,P))$, $(\dagger\dagger\dagger\dagger)$

so from $(\dagger), (\dagger\dagger\dagger\dagger))$, we obtain that;

$2EF = -(\frac{\partial G_{chem'}}{\partial \xi})_{T,P}$

$= -(\Delta G^{\circ}_{chem'} + RTln(Q_{chem'}(T,P)) + \epsilon(T,P))$, $(\sharp)$

Combining $(\sharp), (\dagger\dagger\dagger)$, we obtain that;

$2EF - 2E^{\circ}F = -(\Delta G^{\circ}_{chem'} + RTln(Q_{chem'}(T,P)) + \epsilon(T,P)) - (-\Delta G^{\circ}_{chem'})$

$= -RTln(Q_{chem'}(T,P)) - \epsilon(T,P)$

so that;

$E - E^{\circ} = -\frac{RTln(Q_{chem'}(T,P))}{2F} - \frac{\epsilon(T,P)}{2F}$

□

Lemma 4.2. *At electrical chemical equilibrium (T,P) and (T,P°), and chemical equilibrium (T,P);*

$\Delta G^{\circ} = 2F(E - E^{0})$

Proof. By Lemma 4.1, we have that;

$E - E^{\circ} = -\frac{RTln(Q)}{2F} - \frac{\epsilon(T,P)}{2F}$, $(*)$

and, by Lemma 3.2, we have that;

$0 = (\frac{\partial G}{\partial \xi})_{T,P} = \Delta G^{\circ} + RTln(Q) + \epsilon(T,P)$, $(**)$

Rearranging $(*), (**)$, we obtain the result.

□

Lemma 4.3. *If $\epsilon = 0$, we have, for all $T_1 > 0$, that;*

$(\frac{\partial G}{\partial \xi})_{T,P}|_{(T_1,P_1)} = (\frac{\partial G}{\partial \xi})_{T,P}|_{(T_1,P_1^{\circ})}$

iff;

$E(T_1,P_1) = E(T_1,P_1^{\circ}) = E^{\circ}(T_1)$

where G is the Gibbs energy function for the charged and uncharged species.

Proof. By $(\dagger)$ of Lemma 4.1, we have that;

$(\frac{\partial G}{\partial \xi})_{T,P} = (\frac{\partial G_{chem'}}{\partial \xi})_{T,P} + 2EF$ $(*)$

By Lemma 3.5, we have that $(\frac{\partial G_{chem'}}{\partial \xi})_{T,P}$ is independent of P, in particularly, we have that;

$(\frac{\partial G_{chem'}}{\partial \xi})_{T_1,P_1} = (\frac{\partial G_{chem'}}{\partial \xi})_{T_1,P_1^{\circ}}$ $(**)$

so that, combining $(*), (**)$, we obtain the result. □

Lemma 4.4. *We have, for all $T_1 > 0, P_1 > 0$, that;*

$2F(E(T_1,P_1) - E^{\circ}(T_1)) = (\frac{\partial G}{\partial \xi})_{T,P}|_{(T_1,P_1)} - (\frac{\partial G}{\partial \xi})_{T,P}|_{(T_1,P_1^{\circ})} - RT_1ln(Q(T_1,P_1)) - \epsilon(T_1,P_1)$

Proof. Following the proof of Lemma 4.1, we have that;

$(\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1} = (\frac{\partial G_{chem'}}{\partial \xi})_{T,P}|_{T_1,P_1} + 2E(T_1,P_1)F$ $(*)$

$2E^{\circ}(T_1)F = (\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1^{\circ}} - (\frac{\partial G_{chem'}}{\partial \xi})_{T,P}|_{T_1,P_1^{\circ}}$

$= (\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1^{\circ}} - \Delta G^{\circ}_{chem'}(T_1)$ $(**)$

so from $(*), (**)$ and Lemma 3.2;

$2E(T_1, P_1)F = (\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1} - (\frac{\partial G_{chem'}}{\partial \xi})_{T,P}|_{T_1,P_1}$

$= (\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1} - (\Delta G^{\circ}_{chem'}(T_1) + RT_1 ln(Q_{chem'}(T_1, P_1)) + \epsilon(T_1, P_1))$

$2E(T_1, P_1)F - 2E^{\circ}(T_1)F = (\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1} - (\Delta G^{\circ}_{chem'}(T_1) + RT_1 ln(Q_{chem'}(T_1, P_1)) + \epsilon(T_1, P_1))$

$-((\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1^{\circ}} - \Delta G^{\circ}_{chem'}(T_1))$

$= (\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1} - ((\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1^{\circ}} - RT_1 ln(Q_{chem'}(T_1, P_1)) - \epsilon(T_1, P_1)$

□

5. DILUTE SOLUTIONS

Definition 5.1. *As mentioned in Definition 2.1, we can consider an electrolyte as a solute in a dilute solution. Sometimes the solvent is involved in an electrolytic reaction, for example;*

$2H_2O + 4e^-(R) \to O_2 + 2H_2 + 4e^-(L)$ $(*)$

and sometimes not, as in the standard cell, where we can consider H_2O as the solvent not involved in the reaction. In Lemmas 0.4-0.12, for the standard cell, we can replace Q defined as $\prod_{i=1}^{c} a_i^{\nu_i}$ by $a_0(\prod_{i=1}^{c} a_i^{\nu_i})$, considering H_2O as substance 0.

We ideally have that $\mu_i = \mu_i^{\circ} + RTln(a_i)$, $0 \leq i \leq c$, $(\dagger)$, when we define the activities a_i, for $0 \leq i \leq c$, which, when $(\dagger)$ holds, involves a contradiction.

Lemma 5.2. *In Lemmas 0.4-0.12, for the standard cell, and considering a dilute solution with no interaction of the solvent, replacing Q defined as $\prod_{i=1}^{c} a_i^{\nu_i}$ by;*

$a_0(\prod_{i=1}^{c} a_i^{\nu_i})$

If we assume without approximation that $\mu_i = \mu_i^{\circ} + RTln(a_i)$, $0 \leq i \leq c$, then;

Lemma 2.7; $E - E^{\circ} = -\frac{RTln(Q)}{2F} + \frac{RTln(\frac{a_0(T,P)}{a_0(T,P^{\circ})})}{2F}$

Lemma 2.8; $(\frac{\partial G}{\partial \xi})_{T,P} = \Delta G^\circ + RTln(\frac{Q}{a_0(T,P)})$

where ΔG° *is the Gibbs energy change for* 1 *mole of reaction without the solvent.*

Lemma 2.9; $\Delta G^\circ = 2F(E - E^\circ) + RTln(a_0(T, P^\circ))$

Lemma 2.10; The same with the modification that if chemical and electrical equilibrium exist at (T, P°) *and* (T, P), $Q(T, P) = a_0(T, P)$ *and* $E - E^\circ = -\frac{RTln(a_0(T,P^\circ))}{2F}$. *Conversely, if* $Q(T, P) = \frac{a_0(T,P)}{a_0(T,P^\circ)}$ *and chemical equilibrium exists at* (T, P°) *then chemical equilibrium exists at* (T, P).

Chemical equilibrium exists at (T, P) *iff* $Q(T, P) = a_0 e^{\frac{-\Delta G^\circ}{RT}}$

We always have that $Q(T, P^\circ) = 1$

Lemma 2.11; The same, with the modification that along a chemical equilibrium path, we have that;

$ln(\frac{Q(T_2)}{Q(T_1)}) = \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^\circ}{T^2} dT + ln(\frac{a_0(T_2,P_2)}{a_0(T_1,P_1)})$

and, if ΔH° *is temperature independent;*

$ln(\frac{Q(T_2)}{Q(T_1)}) = -\frac{\Delta H^\circ}{R}(\frac{1}{T_2} - \frac{1}{T_1}) + ln(\frac{a_0(T_2,P_2)}{a_0(T_1,P_1)})$

For $c \in \mathcal{R}$, *if* D_c *intersect the line* $P = P^\circ$ *at* (T_1, P°), *then, for* $(T_2, P) \in D_c$, *we have that;*

$Q(T_2, P) = e^{\frac{\Delta G^\circ(T_1) - \Delta G^\circ(T_2)}{RT_2}} a_0(T_1, P^\circ)^{\frac{-T_1}{T_2}} a_0(T_2, P)$ $(\dagger\dagger\dagger)'$

$c = \Delta G^\circ(T_1) - RT_1 ln(a_0(T_1, P^\circ)$

$ln(\frac{Q(T_2)}{Q(T_1)}) = ln(Q(T_2)) = \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^\circ - c}{T^2} dT + ln(\frac{a_0(T_2,P)}{a_0(T_1,P^\circ)})$

$\frac{\Delta G^\circ(T_2) - \Delta G^\circ(T_1)}{T_2} = -\int_{T_1}^{T_2} \frac{\Delta H^\circ - c}{T^2} dT + R(1 - \frac{T_1}{T_2}) ln(a_0(T_1, P^\circ))$

and if ΔH° *is temperature independent;*

$ln(\frac{Q(T_2)}{Q(T_1)}) = ln(Q(T_2)) = -(\frac{\Delta H^\circ - c}{R})(\frac{1}{T_2} - \frac{1}{T_1}) + ln(\frac{a_0(T_2,P)}{a_0(T_1,P^\circ)})$ $(\dagger\dagger)'$

$\frac{\Delta G^\circ(T_2)-\Delta G^\circ(T_1)}{T_2} = (\Delta H^\circ - c)(\frac{1}{T_2} - \frac{1}{T_1}) + R(1 - \frac{T_1}{T_2})ln(a_0(T_1, P^\circ))$ $(\dagger)'$

to obtain;

$\Delta G^\circ(T_1) = \frac{T_1}{T_2}\Delta G^\circ(T_2) - \Delta H^\circ(\frac{T_1}{T_2} - 1)$

again.

Lemma 2.12; The same, with the modification that if $\epsilon \neq 0$*;*

$Q(T_2, P') = e^{\frac{\epsilon(P'-P'^\circ)}{RT_2}} a_0(T_2, P')$

and the dynamic equilibrium paths are given by;

$a_0(T_2, P')e^{\frac{\epsilon(P'-P'^\circ)}{RT_2}} = c$

for $c \in \mathcal{R}_{\geq 0}$*, while if* $\epsilon = 0$*,* $Q(T_2, P') = \frac{a_0(T_2,P')}{a_0(T_2,P'^\circ)}$*, the dynamic equilibrium lines are given by;*

$\frac{a_0(T_2,P')}{a_0(T_2,P'^\circ)} = c$

for $c \in \mathcal{R}_{\geq 0}$ *and the quasi-chemical equilibrium lines are given by;*

$\lambda + \beta T_2 + \sigma ln(T_2) = c$

for $c \in \mathcal{R}$*.*

Proof. Following the proof of Lemma 2.10, we note that for Gibbs function G with $c+1$ species, including the solvent, substance 0, as $dn_0 = 0$, that;

$dG = \sum_{i=0}^{c} \mu_i dn_i$

$= \sum_{i=1}^{c} \mu_i dn_i$

so the first three claims in Lemma 2.10 go through as before. Going through the proof of Lemma 2.8, we then obtain that;

$(\frac{\partial G}{\partial \xi})_{T,P} = \Delta G^\circ + RTln(\prod_{i=1}^{c} a_i^{\nu_i})$

$= \Delta G^{\circ} + RTln(\frac{\prod_{i=0}^{c} a_i^{\nu_i}}{a_0(T,P)})$

$= \Delta G^{\circ} + RTln(\frac{Q}{a_0(T,P)})$

Going back through the proof of Lemma 2.10, we obtain that $RTln(\frac{Q}{a_0(T,P)}) = 0$, so that $Q(T,P) = a_0(T,P)$. Going through the proof of Lemma 2.7, using the fact that $\mu_i = \mu_i^{\circ} + RTln(a_i)$, for $0 \leq i \leq c$, so that $Q(T,P^{\circ}) = 1$, we have that;

$(\frac{\partial G_{chem'}}{\partial \xi})_{T,P^{\circ}} = \Delta G^{\circ}_{chem'} + RTln(Q_{chem'}(T,P^{\circ})$

$= \Delta G^{\circ}_{chem'} + RTln(\frac{Q}{a_0(T,P^{\circ})})$

$= \Delta G^{\circ}_{chem'} - RTln(a_0(T,P^{\circ}))$ $(\dagger\dagger)'$

where $G_{chem'}$ is the Gibbs energy restricted to the uncharged species without the solvent. Using $(\dagger)$ from Lemma 2.7 and $(\dagger\dagger)'$, we obtain;

$2E^{\circ}F = -\Delta G^{\circ}_{chem'} + RTln(a_0(T,P^{\circ}))$ $(\dagger\dagger\dagger)'$

Similarly, we obtain;

$(\frac{\partial G_{chem'}}{\partial \xi})_{T,P} = \Delta G^{\circ}_{chem'} + RTln(Q_{chem'}(T,P)$

$= \Delta G^{\circ}_{chem'} + RTln(\frac{Q}{a_0(T,P)})$

so that, from $(\dagger)$ from Lemma 2.7;

$2EF = -(\Delta G^{\circ}_{chem'} + RTln(\frac{Q}{a_0(T,P)}))$ $(\sharp)'$

Combining $(\sharp)'$, $(\dagger\dagger\dagger)'$, we obtain;

$2EF - 2E^{\circ}F = -(\Delta G^{\circ}_{chem'} + RTln(\frac{Q}{a_0(T,P)})) - (-\Delta G^{\circ}_{chem'} + RTln(a_0(T,P^{\circ})))$

$= -RTln(\frac{Q}{a_0(T,P)}) - RTln(a_0(T,P^{\circ}))$

$= -RTln(Q) + RTln(\frac{a_0(T,P)}{a_0(T,P^{\circ})})$

which gives the result.of Lemma 2.7. Going back through the proof of Lemma 2.10 again, we then have that;

$$E - E^\circ = -\frac{RTln(Q)}{2F} + \frac{RTln(\frac{a_0(T,P)}{a_0(T,P^\circ)})}{2F}$$

$$= -\frac{RTln(a_0(T,P))}{2F} + \frac{RTln(\frac{a_0(T,P)}{a_0(T,P^\circ)})}{2F}$$

$$= -\frac{RTln(a_0(T,P^\circ))}{2F}$$

For the converse claim, we have by the modification of Lemma 2.8, and the facts that $Q(T,P) = \frac{a_0(T,P)}{a_0(T,P^\circ)}$,$Q(T,P^\circ) = 1$, $(\frac{\partial G}{\partial \xi})_{T,P^\circ} = 0$, that;

$$(\frac{\partial G}{\partial \xi})_{T,P} = \Delta G^\circ + RTln(\frac{Q}{a_0(T,P)})$$

$$= \Delta G^\circ - RTln(a_0(T,P^\circ))$$

$$(\frac{\partial G}{\partial \xi})_{T,P^\circ} = \Delta G^\circ + RTln(\frac{Q}{a_0(T,P^\circ)})$$

$$= 0$$

so that we have chemical equilibrium at (T,P). For the penultimate claim of Lemma 2.10, rearrange the formula from the modification of Lemma 2.8, with the definition of chemical equilibrium;

$$(\frac{\partial G}{\partial \xi})_{T,P} = \Delta G^\circ + RTln(\frac{Q}{a_0(T,P)}) = 0$$

The last claim is clear from;

$\mu_i = \mu_i^\circ + RTln(a_i)$, for $0 \leq i \leq c$

For Lemma 2.9, we have by the modification of Lemma 2.7, that;

$$E - E^\circ = -\frac{RTln(Q)}{2F} + \frac{RTln(\frac{a_0(T,P)}{a_0(T,P^\circ)})}{2F}$$

and, by the modification of Lemma 2.8, that;

$$0 = (\frac{\partial G}{\partial \xi})_{T,P} = \Delta G^\circ + RTln(Q) - RTln(a_0(T,P))$$

so that;

$$\Delta G^\circ = RTln(a_0(T,P)) - RTln(Q)$$

$= RTln(a_0(T,P)) + 2F(E - E^\circ) - RTln(\frac{a_0(T,P)}{a_0(T,P^\circ)})$

$= 2F(E - E^\circ) + RTln(a_0(T,P^\circ))$

For the modification of Lemma 2.11, the first part of the proof goes through with the chemical potentials $\mu_i, 1 \leq i \leq c$, defined relative to the Gibbs energy including the solvent. By the modification of Lemma 2.10, we have that $Q = a_0 e^{\frac{-\Delta G^\circ}{RT}}$ along a chemical equilibrium path, so that $ln(Q) = \frac{-\Delta G^\circ}{RT} + ln(a_0(T,P))$, $(K)'$. It follows that;

$\frac{dln(Q)}{dT} = \frac{d}{dT}(\frac{-\Delta G^\circ}{RT}) + \frac{d}{dT}(ln(a_0(T,P)))$

$= \frac{\Delta H^\circ}{RT^2} + \frac{d}{dT}(ln(a_0(T,P)))$

It follows, integrating between T_1 and T_2, using $(K)'$ and the fundamental theorem of calculus, that;

$ln(\frac{Q(T_2)}{Q(T_1)}) = ln(Q)(T_2) - ln(Q)(T_1)$

$= \frac{-\Delta G^\circ(T_2)}{RT_2} + \frac{\Delta G^\circ(T_1)}{RT_1} + ln(a_0(T_2,P_2)) - ln(a_0(T_1,P_1))$

$= \int_{T_1}^{T_2} \frac{dln(Q)}{dT} dT$

$= \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^\circ}{T^2} + \int_{T_1}^{T_2} \frac{d}{dT}(ln(a_0(T,P)))dT$

$= \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^\circ}{T^2} + ln(a_0(T_2,P_2)) - ln(a_0(T_1,P_1))$ $(P)'$

so that, rearranging, we obtain the first claim. Using the fact, by the modification of Lemma 2.8, that;

$ln(Q(T_2)) = -\frac{\Delta G^\circ(T_2)}{RT_2} + ln(a_0(T_2,P_2))$

$ln(Q(T_1)) = -\frac{\Delta G^\circ(T_1)}{RT_1} + ln(a_0(T_1,P_1))$

we obtain, substituting into $(P)'$, canceling R, and performing the integration, if ΔH° is temperature independent, that;

$\frac{\Delta G^\circ(T_2)}{T_2} - \frac{\Delta G^\circ(T_1)}{T_1} = -\int_{T_1}^{T_2} \frac{\Delta H^\circ}{T^2} = \Delta H^\circ(\frac{1}{T_2} - \frac{1}{T_1})$ $(Q)'$

For the fifth claim, rearrange $(Q)'$. If D_c intersects the line $P = P^\circ$ at (T_1, P°), for the sixth $(\dagger\dagger\dagger)$ and seventh claims, we have, using

the modification of Lemma 2.8 and the fact from Lemma 2.10 that $Q(T_1, P^\circ) = 1$;

$$(\frac{\partial G}{\partial \xi})_{T_2,P} = \Delta G^\circ(T_2) + RT_2 ln(Q(T_2, P)) - RT_2 ln(a_0(T_2, P))$$

$$= (\frac{\partial G}{\partial \xi})_{T_1,P^\circ}$$

$$= \Delta G^\circ(T_1) + RT_1 ln(Q(T_1, P^\circ)) - RT_1 ln(a_0(T_1, P^\circ))$$

$$= \Delta G^\circ(T_1) - RT_1 ln(a_0(T_1, P^\circ)) = c$$

so that, again rearranging, we obtain the result. Along D_c, we have, using Lemma 2.8, that;

$$ln(Q) = \frac{c - \Delta G^\circ}{RT} + ln(a_0(T, P))$$

so that, using the first part;

$$\frac{dln(Q)}{dT} = \frac{d}{dT}(\frac{c - \Delta G^\circ}{RT}) + \frac{d}{dT}(ln(a_0(T, P)))$$

$$= \frac{-c}{RT^2} + \frac{d}{dT}(\frac{-\Delta G^\circ}{RT}) + \frac{d}{dT}(ln(a_0(T, P)))$$

$$= \frac{\Delta H^\circ - c}{RT^2} + \frac{d}{dT}(ln(a_0(T, P)))$$

so that, performing the integration, using the fact that $Q(T_1, P^\circ) = 1$;

$$ln(Q(T_2)) - ln(Q(T_1)) = ln(Q(T_2)) = \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^\circ - c}{T^2} dT + ln(a_0(T_2, P_2)) - ln(a_0(T_1, P^\circ))$$

We have that, by the modification of Lemma 2.8;

$$ln(Q(T_2)) = \frac{c - \Delta G^\circ(T_2)}{RT_2} + ln(a_0(T_2, P))$$

$$ln(Q(T_1)) = 0$$

so that, using the formula for c;

$$ln(Q(T_2)) = ln(Q(T_2)) - ln(Q(T_1))$$

$= \frac{c-\Delta G^\circ(T_2)}{RT_2} + ln(a_0(T_2, P))$

$= \frac{\Delta G^\circ(T_1)-RT_1 ln(a_0(T_1,P^\circ))-\Delta G^\circ(T_2)}{RT_2} + ln(a_0(T_2, P))$

$= \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^\circ - c}{T^2} dT + ln(a_0(T_2, P_2)) - ln(a_0(T_1, P^\circ))$

$= \frac{-1}{R}(\Delta H^\circ - c)(\frac{1}{T_2} - \frac{1}{T_1}) + ln(a_0(T_2, P_2)) - ln(a_0(T_1, P^\circ))$

and rearranging;

$\frac{\Delta G^\circ(T_1)-RT_1 ln(a_0(T_1,P^\circ))-\Delta G^\circ(T_2)}{RT_2} = \frac{-1}{R}(\Delta H^\circ - c)(\frac{1}{T_2} - \frac{1}{T_1}) - ln(a_0(T_1, P^\circ))$

$\frac{\Delta G^\circ(T_2)-\Delta G^\circ(T_1)}{T_2} + \frac{RT_1 ln(a_0(T_1,P^\circ))}{T_2}$

$= (\Delta H^\circ - c)(\frac{1}{T_2} - \frac{1}{T_1}) + Rln(a_0(T_1, P^\circ))$

$\frac{\Delta G^\circ(T_2)-\Delta G^\circ(T_1)}{T_2}$

$= (\Delta H^\circ - c)(\frac{1}{T_2} - \frac{1}{T_1}) + Rln(a_0(T_1, P^\circ)) - \frac{RT_1 ln(a_0(T_1,P^\circ))}{T_2}$

$= (\Delta H^\circ - (\Delta G^\circ(T_1) - RT_1 ln(a_0(T_1, P^\circ))))(\frac{1}{T_2} - \frac{1}{T_1}) + Rln(a_0(T_1, P^\circ)) - \frac{RT_1 ln(a_0(T_1,P^\circ))}{T_2}$

$= (\Delta H^\circ - \Delta G^\circ(T_1))(\frac{1}{T_2} - \frac{1}{T_1}) + RT_1 ln(a_0(T_1, P^\circ))(\frac{1}{T_2} - \frac{1}{T_1}) + (R - \frac{RT_1}{T_2}) ln(a_0(T_1, P^\circ))$

$= (\Delta H^\circ - \Delta G^\circ(T_1))(\frac{1}{T_2} - \frac{1}{T_1}) + ln(a_0(T_1, P^\circ))(RT_1(\frac{1}{T_2} - \frac{1}{T_1}) + (R - \frac{RT_1}{T_2}))$

$= (\Delta H^\circ - \Delta G^\circ(T_1))(\frac{1}{T_2} - \frac{1}{T_1})$

so that, rearranging again;

$\Delta G^\circ(T_1)(\frac{1}{T_1} + \frac{1}{T_2} - \frac{1}{T_2}) = \frac{\Delta G^\circ(T_1)}{T_1}$

$= \frac{\Delta G^\circ(T_2)}{T_2} - \Delta H^\circ(\frac{1}{T_2} - \frac{1}{T_1})$

to obtain;

$\Delta G^\circ(T_1) = \frac{T_1}{T_2}\Delta G^\circ(T_2) - \Delta H^\circ(\frac{T_1}{T_2} - 1)$

For the modification of Lemma 2.12, be careful to use the restricted summation for c substances, in the calculation of $(\frac{\partial(\frac{\partial G}{\partial \xi})_{T,P}}{\partial T})_P$. while the calculation for dU involves $c+1$ substances, including the solvent. If $\epsilon = 0$, we have that;

$c = \Delta G^{\circ}(T_2) + RT_2 ln(Q(T_2, P')) - RT_2 ln(a_0(T_2, P'))$

$= \Delta G^{\circ}(T_2) - RT_2 ln(a_0(T_2, P'^{\circ}))$

so that rearranging, $Q(T_2, P') = \frac{a_0(T_2,P')}{a_0(T_2,P'^{\circ})}$

and the claims about dynamic and quasi-chemical equilibrium lines follows from $Q = c$ and $(\frac{\partial G}{\partial \xi})_{T,P} = c$, for $c \in \mathcal{R}_{\geq 0}$ and $c \in \mathcal{R}$ respectively. If $\epsilon \neq 0$, we use the modification of Lemma 2.8, to obtain the formula for the activity coefficient;

$Q(T_2, P') = e^{\frac{(\frac{\partial G}{\partial \xi})_{T,P}|_{T_2,P'} - \Delta G^{\circ}(T_2) + RT_2 ln(a_0(T_2,P'))}{RT_2}}$

$= e^{\frac{\epsilon(P'-P'^{\circ})}{RT_2}} a_0(T_2, P')$

Again, the determination of the dynamical and quasi-chemical equilibrium lines follows again from rearrangement of $Q = c$ and $(\frac{\partial G}{\partial \xi})_{T,P} = c$, for $c \in \mathcal{R}_{\geq 0}$ and $c \in \mathcal{R}$ respectively.

□

Lemma 5.3. *In Lemmas 0.4-0.12, for the case of a reaction like* $(*)$ *in Definition 5.1, and considering a dilute solution with interaction of the solvent, replacing* Q *defined as* $\prod_{i=1}^{c} a_i^{\nu_i}$ *by;*

$\prod_{i=0}^{c} a_i^{\nu_i}$

If we assume without approximation that $\mu_i = \mu_i^{\circ} + RTln(a_i)$, $0 \leq i \leq c$, *then the proofs go through as before, with the modification that we have* $c+1$ *rather than* c *substances.*

Remarks 5.4. *In the case of a solvent with no interaction, if we define the activities by* $a_i = x_i$, $0 \leq i \leq c$, *with the definition of* Q *as* $a_0 \prod_{1 \leq i \leq c} a_i^{\nu_i}$, *then we need to modify the proofs of Lemmas 2.17 and 2.20. This is done in Lemma 10.4. For the existence of a feasible path, where we require that the* n_0 *term is fixed, see Remark 10.1, we need to change Lemma 2.19. Letting* $d_0 > 0$ *denote the fixed molar amount of*

the solvent, we obtain the relation, modifying the proof of Lemma 2.19;

$$d_0 \prod_{i=1}^{c-1} (\tfrac{\nu_i}{\nu_c} n_c + d_i)^{\nu_i}(t) n_c^{\nu_c}(t) = \epsilon(t)((\sum_{i=1}^{c-1} \tfrac{\nu_i}{\nu_c} + 1)n_c + \sum_{i=0}^{c-1} d_i)^w(t)$$

where $w = 1 + \sum_{i=1}^{c} \nu_i$.

In the $w > 0$ *case, absorb the constant* d_0 *into* $\epsilon(t)$*, by setting* $\epsilon_1(t) = \frac{\epsilon(t)}{d_0} > 0$*, and redefine* $\sigma = \sum_{i=0}^{c-1} d_i$*. Then use the proof of Lemma 2.19, noting that if* $\nu_i = w$*, for* $1 \leq i \leq p$*, then* $w = 1 + \sum_{i=1}^{c} \nu_i > \sum_{i=1}^{p} \nu_i = \sum_{i=1}^{p} w = pw$ *which is a contradiction again. If* $w < 0$*, then use reciprocality again to reduce to* $w > 0$*, replacing* d_0 *with* $\frac{1}{d_0} > 0$*. The* $w = 0$ *case is again similar, using the* $w > 0$ *calculation.*

6. Dilute solutions with Henry's Law for Solutes, Raoult's Law for the Solvent and Interaction of the Solvent

Definition 6.1. *As mentioned in Definition 2.1, we can consider an electrolyte as a solute in a dilute solution and define the activities* a_i*,* $0 \leq i \leq c$*, by;*

$$a_0 = x_0 \simeq 1$$

$$a_i = x_i \ (1 \leq i \leq c)$$

and define;

$$Q = a_0 \prod_{i=1}^{c} a_i^{\nu_i} \simeq \prod_{i=1}^{c} a_i^{\nu_i} \ \textit{(no interaction of the solvent)}$$

$$Q = \prod_{i=0}^{c} a_i^{\nu_i} \ \textit{(interaction of the solvent)}$$

We ideally have that $\mu_i = \mu_i^\circ + RTln(a_i)$*,* $0 \leq i \leq c$*, which involves a contradiction. By Henry's Law, we have that* $P_i = k_i x_i$*,* $1 \leq i \leq c$*, so that, by Henry's Law, phase equilibrium and the ideal gas law;*

$$\mu_i^{(sol)} = \mu_i^{(g)\circ} + RTln(\tfrac{P_i}{P^\circ})$$

$$= \mu_i^{(g)\circ} + RTln(\tfrac{k_i x_i}{P^\circ})$$

$= \mu_i^{(H)\circ} + RTln(x_i)$ $(*)$

where $\mu_i^{(H)\circ} = \mu_i^{(g)\circ} + RTln(\frac{k_i}{P^\circ})$ $(\dagger)$. *From* $(*)$, *we obtain that;*

$\mu_i^\circ = \mu_i^{(H)\circ} + RTln(x_i(T, P^\circ))$ $(\dagger\dagger)$

and, for $1 \leq i \leq c$*;*

$\mu_i = \mu_i^\circ - RTln(x_i(T, P^\circ)) + RTln(x_i)$

$= \mu_i^\circ + RTln(x_i) + \kappa(T)$ $(\dagger\dagger\dagger)$

where, by Henry's law;

$\kappa(T) = -RTln(x_i(T, P^\circ))$

$= -RTln(\frac{P_{i,0}}{k_i})$

$= RTln(\frac{k_i}{P_{i,0}})$

and $P_{i,0}$ is the partial pressure of component i at (T, P°), ([5]).

We can use Raoult's law for the solvent as $P_0 = P_0^* x_0$, see [9]*. Then, using equilibrium with an ideal gas mixture;*

$$\mu_0^{(sol)} = \mu_0^{\circ(g)} + RTln(\frac{P_0}{P^\circ})$$

$$= \mu_0^{\circ(g)} + RTln(\frac{P_0^* x_0}{P^\circ})$$

$$\mu_0^{\circ(g)} + RTln(x_0) + RTln(\frac{P_0^*}{P^\circ})$$

$$= \mu_0^*(T, P_0^*) + RTln(x_0)$$

[5] Another way of looking at the problem in the special case of water electrolysis, is to use the phase rule, and the ideal gas law as an approximation, to write;

$$\mu_i^{(sol)} \simeq \mu_i^{(g)\circ} + RTln(\frac{P_i}{P^\circ})$$

$$= \mu_i^{(sol)\circ} + RTln(\frac{P_i}{P^\circ})$$

If we assume that the equilibrium partial pressures $\{P_{1,0}, P_{2,0}\}$ of hydrogen and oxygen are P° at P°, which seems reasonable if we carry out electrolysis at P° before applying voltage, we obtain that;

$$\mu_i^{(sol)\circ} = \mu_i^{(g)\circ} + RTln(\frac{P_{i,0}}{P^\circ}) = \mu_i^{(g)\circ}.$$

It follows, by Henry's law;

$$\mu_i \simeq \mu_i^\circ + RTln(\frac{k_i x_i}{P^\circ})$$

$$= \mu_i^\circ + RTln(x_i) + RTln(\frac{k_i}{P^\circ})$$

and then;

$$RTln(x_i)(T, P^\circ) \simeq -RTln(\frac{k_i(T,P^\circ)}{P^\circ})$$

$$= RTln(\frac{P^\circ}{k_i(T,P^\circ)})$$

so that;

$$x_i(T, P^\circ) \simeq \frac{P^\circ}{k_i(T,P^\circ)}$$

and the concentrations at P° are approximately determined by $k_i(T, P^\circ)$. We can make this approximation more precise when we consider fugacity.

$= \mu_0^*(T,P) + RTln(x_0) + \theta(T,P)\ (**)$

where $\theta(T,P) = \mu_0^*(T,P_0^*) - \mu_0^*(T,P) \simeq 0$

so that;

$RTln(x_0) = RTln(\frac{P_i}{P^\circ}) - RTln(\frac{P_i^*}{P^\circ})$

and;

$\mu_0 = \mu_0^* + RTln(x_0) + \theta$

$= \mu_0^* + RTln(\frac{P_0}{P^\circ}) - RTln(\frac{P_0^*}{P^\circ}) + \theta\ (***)'$

We also have, using the phase rule for the solvent in equilibrium with an ideal gas mixture, that;

$\mu_0^{(g)} = \mu_0^{\circ(g)} + RTln(\frac{P_0}{P^\circ})$

$\mu_0^{(sol)} = \mu_0^{\circ(sol)} + RTln(\frac{P_0}{P^\circ})\ (*)$

Combining $(*), (***)'$*, we obtain that;*

$\mu_0^* = \mu_0 - RTln(\frac{P_0}{P^\circ}) + RTln(\frac{P_0^*}{P^\circ}) - \theta$

$= (\mu_0^\circ + RTln(\frac{P_0}{P^\circ})) - RTln(\frac{P_0}{P^\circ}) + RTln(\frac{P_0^*}{P^\circ}) - \theta$

$= \mu_0^\circ + RTln(\frac{P_0^*}{P^\circ}) - \theta\ (\dagger)'$

Letting $P_0^* = P^\circ$*, we obtain that* $\mu_0^*(T,P') = \mu_0^\circ - \theta$*, for the corresponding* P'*,* $(****)'$

From $(**)$*,* $(****)'$*, we obtain that;*

$\mu_0 = \mu_0^* + RTln(x_0) + \theta$

$= \mu_0^*(T,P') + \delta + RTln(x_0) + \theta$

$= \mu_0^\circ - \theta + \delta + RTln(x_0) + \theta$

$= \mu_0^\circ + RTln(x_0) + \delta$

where $\delta = \mu_0^*(T,P) - \mu_0^*(T,P') \simeq 0$

Using the same calculation as before, we have that;

$$\mu_0 = \mu_0^\circ + RTln(x_0) + \gamma(T,P)$$

Lemma 6.2. *In the case of dilute solutions, with interaction of the solvent, a feasible path* γ *is a dynamic equilibrium path iff* $pr(\gamma_{12}) \subset C_c$, *for some* $c \in \mathcal{R}_{>0}$ *iff* $\frac{dQ}{dt} = 0$.

Proof. We have that;

$$\prod_{i=0}^{c} a_i^{\nu_i} = \prod_{i=0}^{c} x_i^{\nu_i}$$

$$= Q = c = f$$

where $x_i = \frac{n_i}{n}$. Now follow through the proof of Lemma 2.17, as we are differentiating, the proof works with a constant $f > 0$. □

We reformulate Lemmas 3.2 to 3.6 in this context, assuming Henry's law for the solutes and the solvent an ideal solution;

Lemma 6.3. *In the dilute solution case, with interaction of the solvent, for the energy function* G *involving* $c+1$ *uncharged species;*

$$(\tfrac{\partial G}{\partial \xi})_{T,P} = \Delta G^\circ + RTln(Q) + \epsilon$$

where $\epsilon(T,P) = \nu_0\gamma_0(T,P) + \sum_{i=1}^{c} \nu_i\kappa_i(T) \simeq 0$, $\gamma_0(P) \simeq 0$ *and* $\kappa_i(T) \simeq 0$ *are the error term for the* i*'th uncharged species in Definition 6.1,* $1 \leq i \leq c$.

Proof. The proof is clear from Lemma 3.2.

□

Lemma 6.4. *For a dilute solution, with interaction of the solvent, we have, using the definition of* $\epsilon(T,P)$ *in Lemma 6.3, the error term* $\gamma_0(T,P)$ *and the error terms* $\kappa_i(T)$, $1 \leq i \leq c$ *in Definition 5.1, that the same results as Lemma 3.3 hold, replacing* $\epsilon(T,P)$ *with the new* $\epsilon(T,P)$ *and* $\delta(T)$ *with* $\epsilon(T,P^\circ) = \nu_0\gamma_0(P^\circ) + \sum_{i=1}^{c} \nu_i\kappa_i(T)$, *which we also denote by* $\delta(T)$.

Proof. The proof is clear from the proof of Lemma 3.3.

□

Lemma 6.5. *For a dilute solution, with interaction of the solvent, we have the same result as Lemma 3.4 hold, replacing $\epsilon(T, P(T))$ by the same $\epsilon(T, P(T))$ along the quasi-chemical equilibrium lines.*

Proof. The proof is clear from the proof of Lemma 3.4

□

Lemma 6.6. *For a dilute solution, with interaction of the solvent, we have the same results as Lemma 3.5 hold, replacing $\epsilon(T_1, P')$ by the same $\epsilon(T_1, P')$. In particularly, if $\epsilon \neq 0$, we have that;*

$$Q(T, P) = e^{\frac{\epsilon(P-P^\circ)-\epsilon(T,P)}{RT}}$$

and, if $\epsilon = 0$, we have that;

$$Q(T, P) = e^{\frac{-\epsilon(T,P)}{RT}}$$

Proof. The proof is clear from the proof of Lemma 3.5.

□

Lemma 6.7. *For a dilute solution, with interaction of the solvent, we have that, if $\epsilon \neq 0$;*

$$grad(Q)(T, P) = ((\frac{-\epsilon(P-P^\circ)}{RT^2} + \frac{\epsilon(T,P)}{RT^2} - \frac{\frac{\partial \epsilon}{\partial T}(T,P)}{RT})e^{\frac{\epsilon(P-P^\circ)-\epsilon(T,P)}{RT}},$$

$$(\frac{\epsilon}{RT} - \frac{\frac{\partial \epsilon}{\partial P}(T,P)}{RT})e^{\frac{\epsilon(P-P^\circ)-\epsilon(T,P)}{RT}})$$

and, if $\epsilon = 0$;

$$grad(Q)(T, P) = ((\frac{\epsilon(T,P)}{RT^2} - \frac{\frac{\partial \epsilon}{\partial T}(T,P)}{RT})e^{\frac{-\epsilon(T,P)}{RT}}, \frac{-\frac{\partial \epsilon}{\partial P}(T,P)}{RT}e^{\frac{-\epsilon(T,P)}{RT}})$$

The paths of maximal reaction in the region $|grad(Q)(T, P)| > 1$, $Q(T, P) > 0$, are given by implicit solutions to the differential equations;

$$\frac{dP}{dT} = \frac{\epsilon T - T\frac{\partial \epsilon}{\partial P}(T,P)}{(-\epsilon(P-P^\circ)+\epsilon(T,P)-T\frac{\partial \epsilon}{\partial T}(T,P))}$$

$$\frac{dP}{dT} = \frac{-T\frac{\partial \epsilon}{\partial P}(T,P)}{\epsilon(T,P)-T\frac{\partial \epsilon}{\partial T}(T,P)}$$

respectively.

Proof. The computation of $grad(Q)$ in both cases is a simple application of the chain and product rules. Following the method of Lemma 3.6, noting the claim about maximal reaction is still valid with the same definition of Q, if $\epsilon \neq 0$, we compute;

$$\frac{dP}{dT} = \frac{(\frac{\epsilon}{RT} - \frac{\frac{\partial \epsilon}{\partial P}(T,P)}{RT})e^{\frac{\epsilon(P-P^\circ)-\epsilon(T,P)}{RT}}}{(\frac{-\epsilon(P-P^\circ)}{RT^2} + \frac{\epsilon(T,P)}{RT^2} - \frac{\frac{\partial \epsilon}{\partial T}(T,P)}{RT})e^{\frac{\epsilon(P-P^\circ)-\epsilon(T,P)}{RT}}}$$
$$= \frac{\epsilon T - T\frac{\partial \epsilon}{\partial P}(T,P)}{(-\epsilon(P-P^\circ)+\epsilon(T,P)-T\frac{\partial \epsilon}{\partial T}(T,P))}$$

and, if $\epsilon = 0$;

$$\frac{dP}{dT} = \frac{\frac{-\frac{\partial \epsilon}{\partial P}(T,P)}{RT}e^{\frac{-\epsilon(T,P)}{RT}}}{(\frac{\epsilon(T,P)}{RT^2} - \frac{\frac{\partial \epsilon}{\partial T}(T,P)}{RT})e^{\frac{-\epsilon(T,P)}{RT}}}$$
$$= \frac{-T\frac{\partial \epsilon}{\partial P}(T,P)}{\epsilon(T,P)-T\frac{\partial \epsilon}{\partial T}(T,P)}$$

□

7. Solutions with Fugacity

Lemma 7.1. *In the case of solutions with fugacity, we have that;*

$$(\frac{\partial G}{\partial \xi})_{T,P} = \lambda + \epsilon P + \beta T + \sigma ln(T) + H(T) \ (D)$$

where $\{\beta, \epsilon, \lambda, \sigma\} \subset \mathcal{R}$, $H(T)$ *is a function of* T.

Proof. The proof is similar to that of Lemma 2.12, except that we have to add correction terms for mixtures and use the van der Waals equation for real gases. As before, by Lemma 2.10 and the proof of Lemma 2.11, we have that;

$$(\frac{\partial(\frac{dG}{d\xi})_{T,P}}{\partial T})_P = (\frac{\partial(\sum_{i=1}^c \nu_i \mu_i)}{\partial T})_P$$

$$= \sum_{i=1}^c \nu_i (\frac{\partial \mu_i}{\partial T})_P$$

$$= \sum_{i=1}^c \nu_i (\frac{\partial \mu_i}{\partial T})_{P,n}$$

$$= -\sum_{i=1}^c \nu_i \overline{S}_{m,i} \ (*)$$

To compute $\overline{S}_{m,i}$, we have by the first law of thermodynamics;

$dQ = dU + dL = dU + pdV$

where L is the work done by the system, see [5]. We have that;

$\Delta H_{mix} = -\sum_{i=1}^{c} n_i RT^2 (\frac{\partial ln(\gamma_i)}{\partial T})_{P,n}$

$\Delta V_{mix} = \sum_{i=1}^{c} n_i RT (\frac{\partial ln(\gamma_i)}{\partial P})_{T,n}$

see [9], where $\gamma_i(T, P)$ are the activity coefficients, so that;

$\Delta U_{mix} = \Delta H_{mix} + P\delta V_{mix}$

$= -\sum_{i=1}^{c} n_i RT^2 (\frac{\partial ln(\gamma_i)}{\partial T})_{P,n} + \sum_{i=1}^{c} n_i RTP (\frac{\partial ln(\gamma_i)}{\partial P})_{T,n}$

$= \theta_1(\overline{n}, T, P) + P\theta_2(\overline{n}, T, P)$

$= \theta(\overline{n}, T, P)$

and we are using convention (I) of [9]. That is $U_{mix} = \sum_{i=1}^{c} U_i + \theta(\overline{n}, T, P)$.

Again, we assume that component i is in thermal equilibrium T with an ideal gas at pressures (P, P_i^*). Then at constant (T, P, P_i^*), we have that, as before;

$dG_{i,liq} = dU_{i,liq} + PdV_{i,liq} - TdS_{i,liq}$

$= -dG_{i,gas} = -dU_{i,gas} - P_i^* dV_{i,gas} + TdS_{i,gas}$

$= dH_{i,liq} - TdS_{i,liq} = -dH_{i,gas} + TdS_{i,gas}$

so that;

$d(H_{i,liq} + H_{i,gas}) = TdS_{i,liq} + TdS_{i,gas}$

and;

$dU_{i,liq} + PdV_{i,liq} + dU_{i,gas} + P_i^* dV_{i,gas} = d(H_{i,liq} + H_{i,gas})$

Integrating between the initial and final states of no evaporation and complete evaporation, we obtain that;

$$-U_{i,liq} - PV_{i,liq} + U_{i,gas} + P_i^* V_{i,gas} = H_{i,gas} - H_{i,liq} = \Delta H_{i,vap}$$

so that, rearranging;

$$U_{i,liq}(T, P, n_i) = U_{i,gas} - \Delta H_{i,vap} - PV_{i,liq} + P_i^* V_{i,gas}$$

It follows, as $V_{mix} = \theta_2(\overline{n}, T, P)$ for a non-ideal mixture, and using the van der Waals equation;

$$(P + \tfrac{a_i n_i^2}{V})(V - n_i b_i) = n_i RT \ (1 \leq i \leq c)$$

for the real gas components, and the calculation of internal energy for a real gas;

$$dU_{i,gas} = n_i C_{V,i} dT - (P - T(\tfrac{\partial P}{\partial T})_V) dV$$

$$= n_i C_{V,i} dT - \tfrac{-a_i n_i^2}{V} dV$$

$$U_{i,gas} = n_i C_{V,i} T + \theta_{3,i}(n_i, T, P) \ (\dagger)$$

where $C_{V,i}$ is the molar heat capacity at constant volume, that;

$$U_{mix,liq}(T, P, \overline{n}) = \textstyle\sum_{i=1}^{c} U_{i,liq}(T, P, n_i) + \theta(\overline{n}, T, P)$$

$$= \textstyle\sum_{i=1}^{c} U_{i,gas} - \sum_{i=1}^{c} \Delta H_{i,vap} - P \sum_{i=1}^{c} V_{i,liq} + \sum_{i=1}^{c} P_i^* V_{i,gas} + \theta(\overline{n}, T, P)$$

$$= \textstyle\sum_{i=1}^{c} U_{i,gas} - \sum_{i=1}^{c} \Delta H_{m,i,vap} n_i - P(V_{liq} - \theta_2(\overline{n}, T, P))$$

$$+ \textstyle\sum_{i=1}^{c} P_i^* \alpha(T, P_i^*, n_i) + \theta(\overline{n}, T, P)$$

where α is obtained by solving the van der Waals equation for $V_{i,gas}$. We can write the equilibrium pressure P_i^* as a function $\beta_i(T, P)$, and use $(\dagger)$, to obtain;

$$U_{mix,liq}(T, P, \overline{n}) = \textstyle\sum_{i=1}^{c} (n_i C_{V,i} T + \theta_{3,i}(n_i, T, P)) - \sum_{i=1}^{c} \Delta H_{m,i,vap} n_i$$

$$-PV_{liq} + \theta_2(\overline{n}, T, P))$$

$$+ \textstyle\sum_{i=1}^{c} \beta_i(T, P) \alpha(T, \beta(T, P), n_i) + \theta(\overline{n}, T, P)$$

$= \sum_{i=1}^{c}(n_i C_{V,i} T - \sum_{i=1}^{c} \Delta H_{m,i,vap} n_i - PV_{liq} + \delta(\overline{n}, T, P)$

$dU_{mix,liq} = \sum_{i=1}^{c} C_{V,i} T dn_i + \sum_{i=1}^{c} C_{V,i} n_i dT - \sum_{i=1}^{c} \Delta H_{m,i,vap} dn_i$

$-V_{liq} dP - P dV_{liq} + \sum_{i=1}^{c} \delta_i(\overline{n}, T, P) dn_i + \gamma_1(\overline{n}, T, P) dT + \gamma_2(\overline{n}, T, P) dP$

$dQ_{mix,liq} = dU_{mix,liq} + P dV_{liq}$

$= \sum_{i=1}^{c} C_{V,i} T dn_i + \sum_{i=1}^{c} C_{V,i} n_i dT - \sum_{i=1}^{c} \Delta H_{m,i,vap} dn_i$

$-V_{liq} dP + \sum_{i=1}^{c} \delta_i(\overline{n}, T, P) dn_i + \gamma_1(\overline{n}, T, P) dT + \gamma_2(\overline{n}, T, P) dP$

$\frac{dQ_{mix,liq}}{T} = \sum_{i=1}^{c} C_{V,i} dn_i + \sum_{i=1}^{c} C_{V,i} n_i \frac{dT}{T} - \sum_{i=1}^{c} \Delta H_{m,i,vap} \frac{dn_i}{T}$

$-V_{liq} \frac{dP}{T} + \sum_{i=1}^{c} \delta_i(\overline{n}, T, P) \frac{dn_i}{T} + \gamma_1(\overline{n}, T, P) \frac{dT}{T} + \gamma_2(\overline{n}, T, P) \frac{dP}{T}$

It follows that;

$\overline{S}_{m,i} = \int_{\Delta n_i = 1} (\frac{dQ}{T})_{n', T, P}$

$= \sum_{i=1}^{c} C_{V,i} - \sum_{i=1}^{c} \frac{\Delta H_{m,i,vap}}{T} + \sum_{i=1}^{c} \frac{\delta_i(\overline{n}, T, P)}{T}$

$= C_{V,i} - \frac{\Delta H_{m,i,vap}}{T} + G_i(T, P)$

where $G_i(T, P) = \frac{\delta_i(\overline{n}, T, P)}{T}$ is independent of $\overline{n}$.

So that, from $(**)$;

$(\frac{\partial(\frac{dG}{d\xi})_{T,P}}{\partial T})_P = -\sum_{i=1}^{c} \nu_i (C_{V,i} - \frac{\Delta H_{m,i,vap}}{T} + G_i(T, P)),\ (***)$

and we assume that $C_{V,i}$ and $\Delta H_{m,i,vap}$ are independent of (T, P). From $(***)$, we see that $(\frac{dG}{d\xi})_{T,P}$ is of the form $\alpha(P) + \beta T + \sigma ln(T) + \int G(T, P) dT$, (B), where $\{\beta, \sigma\} \subset \mathcal{R}$, and, assuming that $(\frac{dG}{d\xi})_{T,P}$ is differentiable, $\alpha \in C^1(\mathcal{R})$. By a similar calculation, we have that;

$(\frac{\partial(\frac{dG}{d\xi})_{T,P}}{\partial P})_T = (\frac{\partial(\sum_{i=1}^{c} \nu_i \mu_i)}{\partial P})_T$

$= \sum_{i=1}^{c} \nu_i (\frac{\partial \mu_i}{\partial P})_T$

$= \sum_{i=1}^{c} \nu_i (\frac{\partial \mu_i}{\partial P})_{T,n}$

$= \sum_{i=1}^{c} \nu_i (\frac{\partial V}{\partial n_i})_{T,P,n'}$

$= \sum_{i=1}^{c} \nu_i \overline{V}_{m,i}$

$= \sum_{i=1}^{c} \nu_i \frac{N_A m_i}{\kappa_i(T,P)}$ (A)

where κ_i is the density of substance i, m_i is the molecular mass, and we assume that $\overline{V}_{m,i}$ is independent of (T, P). We have, from (A, B), that;

$(\frac{\partial (\frac{dG}{d\xi})_{T,P}}{\partial P})_T = \epsilon = \alpha'(P) + \int G_P(T,P)dT$ (AA)

where $\epsilon = \sum_{i=1}^{c} \nu_i \overline{V}_{m,i}$, so that, differentiating with respect to T;

$G_P(T,P) = 0$

$G(T,P) = G(T)$

$\alpha(P) = \lambda + \epsilon P$

and;

$(\frac{dG}{d\xi})_{T,P}$ is of the form;

$\alpha(P) + \beta T + \sigma ln(T) + H(T)$

$= \lambda + \epsilon P + \beta T + \sigma ln(T) + H(T)$ (D)

where $\{\beta, \epsilon, \lambda, \sigma\} \subset \mathcal{R}$.

□

Lemma 7.2. *In the case of solutions with fugacity, we have that;*

$(\frac{\partial G}{\partial \xi})_{T,P} = \lambda + \epsilon P + \beta T$ (E)

where $\{\beta, \epsilon, \lambda\} \subset \mathcal{R}$. *That is, in Lemma 7.1,* $\sigma = H(T) = 0$

Proof. The proof follows from Lemma 3.5, equating coefficients, even when error terms are introduced, and from Lemma 5.1, to cover the case with no interaction of the solvent, and the new definition of the activity coefficient Q.

□

In the case of electrolysis of steam, it is unreasonable to assume that $\overline{V}_{m,i}$ is independent of (T, P), however, we can do a more accurate calculation.

Lemma 7.3. *Electrolysis of steam*

Proof. We assume that the mixture of steam, hydrogen and oxygen is an ideal gas mixture, and consider the fuel cell reaction $2H^2 + O_2 \rightarrow 2H_2O$. We have that, using Dalton's law of partial pressures;

$\mu_i^{(g)} = \mu_i^{(g),\circ} + RTln(\frac{P_i}{P^\circ}) + \epsilon_i(T)$

where;

$\epsilon_i(T) = -RTln(\frac{P_{i,\circ}}{P^\circ}) = -RTln(x_i^\circ(T))$, $P_{i,\circ}$ is the partial pressure of component i at P°, so that;

$\mu_i^{(g)} = \mu_i^{(g),\circ} + RTln(\frac{P_i}{P}) + RTln(\frac{P}{P^\circ}) - RTln(\frac{P_{i,\circ}}{P^\circ})$

$= \mu_i^{(g),\circ} + RTln(x_i) + RTln(\frac{P}{P^\circ}) - RTln(\frac{P_{i,\circ}}{P^\circ})$

$= \mu_i^{(g),\circ} + RTln(x_i) + \delta_i(T, P)$

We have that;

$\frac{\partial \frac{\partial G}{\partial \xi}|_{T,P,\overline{n}}}{\partial P} = \sum_{i=1}^3 \nu_i V_{m,i}$

where, using the ideal gas law;

$V_{m,i} = \frac{\partial V}{\partial n_i}$

$= \frac{\partial (\sum_{j=1}^3 n_j)\frac{RT}{P}}{\partial n_i}$

$= \frac{RT}{P}$

so that;

$\sum_{i=1}^3 \nu_i V_{m,i} = -\frac{RT}{P}$

$\frac{\partial G}{\partial \xi}|_{T,P,\overline{n}} = -RTln(P) + \alpha(T, \overline{n})$

We have that;

$$Q(T,P) = e^{\frac{\frac{\partial G}{\partial \xi}(T,P) - \frac{\partial G}{\partial \xi}(T,P^\circ) - \sum_{i=1}^3 \nu_i \delta_i(T,P)}{RT}}$$

$$= e^{\frac{-RTln(\frac{P}{P^\circ}) - \sum_{i=1}^3 \nu_i (RTln(\frac{P}{P^\circ}) - RTln(\frac{P_{i,\circ}}{P^\circ}))}{RT}}$$

$$= e^{\frac{-RTln(\frac{P}{P^\circ}) + RTln(\frac{P}{P^\circ}) + \sum_{i=1}^3 \nu_i RTln(\frac{P_{i,\circ}}{P^\circ})}{RT}}$$

$$= e^{\frac{\sum_{i=1}^3 \nu_i RTln(\frac{P_{i,\circ}}{P^\circ})}{RT}}$$

$$= \prod_{i=1}^3 x_i^{\nu_i}(T,P^\circ)$$

so that the equilibrium coefficient with error terms is independent of pressure, and no substance is formed keeping temperature fixed. Moreover, as explained above, it is insufficient to determine the amount of substance formed during the reaction. However, with initial molar amounts $\{n_{10}, n_{20}, n_{30}\}$ at (T_0, P°), we have that, by the ideal gas equation;

$$n(T,P^\circ) = n_0 - \xi = \frac{PV}{RT}$$

so that, by the above, PV is fixed at fixed temperature. We have that, as substance formed is independent of pressure;

$$\xi = n_0 - \frac{P^\circ V(T,P^\circ)}{RT}$$

Without error terms, we have that;

$$Q'(T,P) = \frac{P^\circ}{P}$$

which is independent of temperature.

The Nernst equation, which does not use error terms, then becomes;

$$W(T,P) - W^\circ(T) = -\frac{RTln(Q')}{4F}$$

$$= -\frac{RTln(\frac{P^\circ}{P})}{4F}$$

so that, at fixed pressure $2P^\circ$, voltage W has an effect on temperature;

$$W - W^\circ(T) = \frac{2RT}{4F}$$

$$T = \frac{2F}{R}(W - W^\circ(T))$$

$$\xi = n_0 - \frac{2P^\circ V(\frac{2F}{R}(W - W^\circ(T)), 2P^\circ)}{2FR(W - W^\circ(T))}$$

Note that a similar pressure dependence for Q' without error terms is found in [6].

□

8. Dilute solutions with Fugacity and Interaction of the Solvent

Definition 8.1. *As mentioned in Definition 2.1, we can consider an electrolyte as a solute in a dilute solution and define the activities* a_i, $0 \leq i \leq c$, *by;*

$$a_0 = \gamma_0 x_0 \simeq 1$$

$$a_i = \gamma_i x_i \ (1 \leq i \leq c)$$

We can define the activity coefficient $Q = a_0 \prod_{i=1}^{c} a_i^{\nu_i} \simeq \prod_{i=1}^{c} a_i^{\nu_i}$, *but we will adopt a new convention, see below.*

We have that $\mu_i = \mu_i^\circ + RTln(a_i)$, $0 \leq i \leq c$, *which involves the contradiction with the definition of activity for ideal solutions. By the approximation of Henry's Law for the solutes, we have that* $P_i = k_i x_i \gamma_i$, $1 \leq i \leq c$, *(convention (II)), see* [9], *so that, by the approximation of*

Henry's Law, phase equilibrium and the gas law with fugacity δ_i,([6]),;

$\mu_i^{(sol)} = \mu_i^{(g)\circ} + RTln(\frac{\delta_i P_i}{P^\circ})$

$= \mu_i^{(g)\circ} + RTln(\frac{k_i x_i \gamma_i}{P^\circ}) + RTln(\delta_i(T,P))$

$= \mu_i^{(H)\circ} + RTln(\gamma_i x_i) + RTln(\delta_i(T,P))$ $(*)$

where $\mu_i^{(H)\circ} = \mu_i^{(g)\circ} + RTln(\frac{k_i}{P^\circ})$ $(\dagger)$. *From* $(*)$, *we obtain that;*

$\mu_i^\circ = \mu_i^{(H)\circ} + RTln(\gamma_i x_i(T,P^\circ)) + RTln(\delta_i(T,P^\circ)$ $(\dagger\dagger)$

and, for $1 \leq i \leq c$;

$\mu_i = \mu_i^\circ - RTln(\gamma_i x_i(T,P^\circ)) - RTln(\delta_i(T,P^\circ) + RTln(\gamma_i x_i) + RTln(\delta_i(T,P))$

$= \mu_i^\circ + RTln(\gamma_i x_i) + \kappa(T,P)$ $(\dagger\dagger\dagger)$

---

[6] Again, as above, we can make a calculation for electrolysis involving fugacity;

We have that, using the phase rule for the solutes hydrogen and oxygen, the fact that the gases are dissolved, so that the partial pressures match the pressure of the solution, and the approximation of Henry's law;

$\mu_i^{(sol)} = \mu_i^{(g)\circ} + RTln(\frac{\delta_i P_i}{P^\circ})$

$\mu_i^{(sol)\circ} = \mu_i^{(g)\circ} + RTln(\frac{\delta_i P^\circ}{P^\circ})$

$= \mu_i^{(g)\circ} + RTln(\delta_i)(T,P^\circ)$

so that;

$\mu_i^{(sol)} = \mu_i^{(sol)\circ} - RTln(\delta_i)(T,P^\circ) + RTln(\frac{\delta_i P_i}{P^\circ})$

$= \mu_i^{(sol)\circ} + RTln(\frac{\delta_i(T,P)}{\delta_i(T,P^\circ)}) + RTln(\frac{k_i x_i \gamma_i}{P^\circ})$

$= \mu_i^{(sol)\circ} + RTln(x_i) + RTln(\frac{\delta_i(T,P)}{\delta_i(T,P^\circ)}) + RTln(\frac{k_i \gamma_i}{P^\circ})$

so that $x_i(T,P^\circ) = \frac{P^\circ}{k_i \gamma_i(T,P^\circ)}$

and we see that the concentrations at standard pressure are determined again by the constant k_i in Henry's law and the deviation γ_i at standard pressure.

where, from phase equilibrium and $(\dagger), (\dagger\dagger)$*;*

$$\kappa(T,P) = -RTln(\gamma_i x_i(T,P^\circ)) + RT(ln(\delta_i(T,P)) - ln(\delta_i(T,P^\circ))$$

$$= \mu_i^{(H)\circ} - \mu_i^\circ + RTln(\delta_i(T,P^\circ)) + RTln(\tfrac{\delta_i(T,P)}{\delta_i(T,P^\circ)})$$

$$= \mu_i^{(g)\circ} + RTln(\tfrac{k_i}{P^\circ}) - \mu_i^{(sol)\circ} + RTln(\delta_i(T,P))$$

$$= RTln(\tfrac{k_i}{P^\circ}) + RTln(\delta_i(T,P))$$

$$= RTln(\tfrac{k_i\delta_i(T,P)}{P^\circ})$$

We can measure the correction in Raoult's law for the solvent by $P_0 = \gamma_0 P_0^* x_0$*, (convention I), see* [9]*. Then, using the gas law with fugacity* δ_0*, and the correction* σ *for the difference of the chemical potential between a gas in a non ideal mixture and on its own, we have, at equilibrium, that;*

$$\mu_0^{(sol)} = \mu_0^{\circ(g)} + RTln(\tfrac{\delta_0 P_0}{P^\circ})$$

$$= \mu_0^{\circ(g)} + RTln(\tfrac{\delta_0\gamma_0 P_0^* x_0}{P^\circ})$$

$$\mu_0^{\circ(g)} + RTln(\gamma_0 x_0) + RTln(\tfrac{\delta_0 P_0^*}{P^\circ})$$

$$= \mu_0(T,P_0^*) + RTln(\gamma_0 x_0)$$

$$= \mu_0^*(T,P_0^*) + \sigma(T,P_0^*) + RTln(\gamma_0 x_0)$$

$$= \mu_0^*(T,P) + RTln(\gamma_0 x_0) + \theta(T,P)\ (**)$$

where $\theta(T,P) = \mu_0^*(T,P_0^*) - \mu_0^*(T,P) + \sigma(T,P_0^*)$

so that;

$$RTln(\gamma_(0)x_0) = RTln(\tfrac{\delta_0 P_0}{P^\circ}) - RTln(\tfrac{\delta_0 P_0^*}{P^\circ})$$

and;

$$\mu_0 = \mu_0^* + RTln(\gamma_0 x_0) + \theta$$

$$= \mu_0^* + RTln(\tfrac{\delta_0 P_0}{P^\circ}) - RTln(\tfrac{\delta_0 P_0^*}{P^\circ}) + \theta\ (***)'$$

We also have, using the phase rule for the solvent in equilibrium, that;

$\mu_0^{(g)} = \mu_0^{\circ(g)} + RTln(\frac{\delta_0 P_0}{P^\circ})$

$\mu_0^{(sol)} = \mu_0^{\circ(sol)} + RTln(\frac{\delta_0 P_0}{P^\circ})$ $(*)$

Combining $(*), (***)'$*, we obtain that;*

$\mu_0^* = \mu_0 - RTln(\frac{\delta_0 P_0}{P^\circ}) + RTln(\frac{\delta_0 P_0^*}{P^\circ}) - \theta$

$= (\mu_0^\circ + RTln(\frac{\delta_0 P_0}{P^\circ})) - RTln(\frac{\delta_0 P_0}{P^\circ}) + RTln(\frac{\delta_0 P_0^*}{P^\circ}) - \theta$

$= \mu_0^\circ + RTln(\frac{\delta_0 P_0^*}{P^\circ}) - \theta$ $(\dagger)'$

Letting $\delta_0 P_0^* = P^\circ$*, we obtain that* $\mu_0^*(T, P') = \mu_0^\circ - \theta$*, for the corresponding* P'*,* $(****)'$

From $(**)$*,* $(****)'$*, we obtain that;*

$\mu_0 = \mu_0^* + RTln(\gamma_0 x_0) + \theta$

$= \mu_0^*(T, P') + \delta + RTln(\gamma_0 x_0) + \theta$

$= \mu_0^\circ - \theta + \delta + RTln(\gamma_0 x_0) + \theta$

$= \mu_0^\circ + RTln(\gamma_0 x_0) + \delta$

where $\delta = \mu_0^*(T, P) - \mu_0^*(T, P') \simeq 0$

Using the same calculation as before, we have that;

$\mu_0 = \mu_0^\circ + RTln(\gamma_0 x_0) + \lambda(P)$

We can define a new activity coefficient by $Z = \prod_{i=0}^{c} b_i^{\nu_i}$*, where;*

$b_0 = x_0$

$b_i = x_i$*,* $1 \leq i \leq c$

From the above, we have that;

$\mu_0(T,P) = \mu_0^\circ + RTln(x_0) + RTln(\gamma_0(T,P)) + \delta_0(P)$

$= \mu_0^\circ + RTln(b_0) + \phi_0(T,P)$

and, for $1 \leq i \leq c$*;*

$\mu_i(T,P) = \mu_i^\circ + RTln(x_i) + RTln(\gamma_i(T,P)) + \kappa_i(T)$

$= \mu_i^\circ + RTln(b_i) + \psi_i(T,P)$

Lemma 8.2. *In the case of dilute solutions, with interaction of the solvent, a feasible path* γ *is a dynamic equilibrium path iff* $pr(\gamma_{12}) \subset C_f$*, for some* $f \in \mathcal{R}_{>0}$ *iff* $\frac{dZ}{dt} = 0$*.*

Proof. We have that;

$\prod_{i=0}^c a_i^{\nu_i} = \prod_{i=0}^c x_i^{\nu_i}$

$= Z = f$

Now copy the proof of Lemma 6.2.

□

We reformulate Lemmas 3.2 to 3.6 in this context, assuming the approximation to Henry's law for the solutes and the approximation to Raoult's law for the solvent;

Lemma 8.3. *In the dilute solution case, with interaction of the solvent, for the energy function* G *involving* $c+1$ *uncharged species;*

$(\frac{\partial G}{\partial \xi})_{T,P} = \Delta G^\circ + RTln(Z) + \epsilon(T,P)$

where $\epsilon(T,P) = \nu_0\phi_0(T,P) + \sum_{i=1}^c \nu_i\psi_i(T,P)$*, and* ϕ_0 *is the error term for the solvent in Definition 8.1, and* ψ_i*, for* $1 \leq i \leq c$ *are the error terms for the solutes in Definition 8.1.*

Proof. The proof is clear from Lemma 3.2.

□

Lemma 8.4. *For a dilute solution, with interaction of the solvent, we have, using the definition of* $\epsilon(T,P)$ *in Lemma 8.3, the error term* $\phi_0(T,P)$ *and the error terms* $\psi_i(T,P)$*,* $1 \leq i \leq c$ *in Definition 8.1, that the same results as Lemma 3.3 hold, replacing* $\epsilon(P)$ *with* $\epsilon(T,P)$

and δ *with* $\epsilon(T, P^\circ) = \nu_0\phi_0(T, P^\circ) + \sum_{i=1}^{c} \nu_i\psi_i(T, P^\circ)$

Proof. The proof is clear from the proof of Lemma 3.3.

□

Lemma 8.5. *For a dilute solution, with interaction of the solvent, we have the same result as Lemma 3.4 hold, replacing* $\epsilon(P(T))$ *by* $\epsilon(T, P(T))$ *along the quasi-chemical equilibrium lines.*

Proof. The proof is again clear from the proof of Lemma 3.4

□

Lemma 8.6. *For a dilute solution, with interaction of the solvent, we have the same results as Lemma 3.5 hold, replacing* $\epsilon(P')$ *by* $\epsilon(T_1, P')$. *In particularly, if* $\epsilon \neq 0$, *we have that;*

$$Z(T, P) = e^{\frac{\epsilon(P-P^\circ)-\epsilon(T,P)}{RT}}$$

and, if $\epsilon = 0$, *we have that;*

$$Z(T, P) = e^{\frac{-\epsilon(T,P)}{RT}}$$

Proof. The proof is again clear from the proof of Lemma 3.5.

□

Lemma 8.7. *For a dilute solution, with interaction of the solvent, we have that, if* $\epsilon \neq 0$*;*

$$grad(Z)(T, P) = ((\frac{-\epsilon(P-P^\circ)}{RT^2} + \frac{\epsilon(T,P)}{RT^2} - \frac{\frac{\partial\epsilon}{\partial T}(T,P)}{RT})e^{\frac{\epsilon(P-P^\circ)-\epsilon(T,P)}{RT}},$$

$$(\frac{\epsilon}{RT} - \frac{\frac{\partial\epsilon}{\partial P}(T,P)}{RT})e^{\frac{\epsilon(P-P^\circ)-\epsilon(T,P)}{RT}})$$

and, if $\epsilon = 0$*;*

$$grad(Z)(T, P) = ((\frac{\epsilon(T,P)}{RT^2} - \frac{\frac{\partial\epsilon}{\partial T}(T,P)}{RT})e^{\frac{-\epsilon(T,P)}{RT}}, \frac{-\frac{\partial\epsilon}{\partial P}(T,P)}{RT}e^{\frac{-\epsilon(T,P)}{RT}})$$

The paths of maximal reaction in the region $|gradZ(T, P)| > 1$, $Z(T, P) > 0$, *are given by implicit solutions to the differential equations;*

$$\frac{dP}{dT} = \frac{\epsilon T - T\frac{\partial\epsilon}{\partial P}(T,P)}{(-\epsilon(P-P^\circ)+\epsilon(T,P)-T\frac{\partial\epsilon}{\partial T}(T,P))}$$

$\frac{dP}{dT} = \frac{-T\frac{\partial \epsilon}{\partial P}(T,P)}{\epsilon(T,P) - T\frac{\partial \epsilon}{\partial T}(T,P)}$

respectively.

Proof. The proof is the same as Lemma 6.7, replacing Q by Z, noting that Z is defined the same way in terms of activities.

□

9. Electrochemistry with Error Terms, Fugacity and Interaction of the Solvent

Using the new error term $\epsilon(T, P)$ and the activity coefficient Z from Section 8, we have that;

Lemma 9.1. *The Nernst Equation for Catalyzers*

At electrical chemical equilibrium (T, P) *and* (T, P°)*;*

$(E - E^\circ)(T, P) = -\frac{RTln(Z(T,P))}{4F} - \frac{\epsilon(T,P)}{4F}$

Proof. Just follow the proof of Lemma 4.1, replacing $\epsilon(P)$ with $\epsilon(T, P)$ and use the fact that the catalyzer reaction $2H_2O + 4e^-(R) \to O_2 + 2H_2 + 4e^-(L)$ occurs with 4 electrons rather than 2.

□

Lemma 9.2. *At electrical chemical equilibrium* (T, P) *and* (T, P°)*, and chemical equilibrium* (T, P)*;*

$\Delta G^\circ = 4F(E - E^0)$

Proof. Follow the proof of Lemma 4.2, replacing $\epsilon(P)$ with $\epsilon(T, P)$, noting the remark in Lemma 9.1.

□

Lemma 9.3. *If* $\epsilon = 0$*, we have, for all* $T_1 > 0$*, that;*

$(\frac{\partial G}{\partial \xi})_{T,P}|_{(T_1,P_1)} = (\frac{\partial G}{\partial \xi})_{T,P}|_{(T_1,P_1^\circ)}$

iff;

$$E(T_1, P_1) = E(T_1, P_1^\circ) = E^\circ(T_1)$$

where G is the Gibbs energy function for the charged and uncharged species.

Proof. Follow the proof of Lemma 4.3, replacing the result of Lemma 1.5, that $(\frac{\partial G_{chem'}}{\partial \xi})_{T,P}$ is independent of P, with the corresponding same result in Lemma 8.6. □

Lemma 9.4. *We have, for all $T_1 > 0, P_1 > 0$, that;*

$$4F(E(T_1, P_1) - E^\circ(T_1)) = (\frac{\partial G}{\partial \xi})_{T,P}|_{(T_1,P_1)} - (\frac{\partial G}{\partial \xi})_{T,P}|_{(T_1,P_1^\circ)} - RT_1 ln(Z(T_1, P_1)) - \epsilon(T_1, P_1) \ (*)$$

Proof. Follow the proof of Lemma 4.4, replacing $\epsilon(P)$ with $\epsilon(T, P)$.

□

Remarks 9.5. *The result of Lemma 9.4 combined with the determination of the activity coefficient Z in Lemma 8.6 and the error term $\epsilon(T, P)$ in Lemma 8.3 can be use to determine the unknown quantity $(\frac{\partial G}{\partial \xi})_{T,P}$. We can measure the potential difference between the cathode and anode along the dynamical equilibrium paths provided by Lemma 8.6 and then use the formula $(*)$ in Lemma 9.4. Once this is determined, we then alter the power supply, in accordance with $(*)$, to push the reaction along the paths of maximal reaction given in Lemma 8.7. This should improve the efficiency of the production of hydrogen and oxygen, in the case of the electrolyzer reaction, given by $2H_2O + 4e^-(R) \to O_2 + 2H_2 + 4e^-(L)$.*

10. Dilute solutions with Henry's Law for Solutes, Raoult's Law for the Solvent and No Solvent Interaction

As mentioned in Definition 2.1, we can consider an electrolyte as a solute in a dilute solution and define the activities a_i, $0 \leq i \leq c$, by;

$$a_0 = x_0 \simeq 1$$

$$a_i = x_i \ (1 \leq i \leq c)$$

We can either define the activity coefficient by;

$W = \prod_{i=1}^{c} a_i^{\nu_i}$

or, use the more conventional definition;

$Q = a_0 \prod_{i=1}^{c} a_i^{\nu_i} \simeq \prod_{i=1}^{c} a_i^{\nu_i}$

We will consider both cases.

Remarks 10.1. *In the first case, if a_0 is assumed constant, we have to redefine a feasible path by using coordinates $(T, P, n_0, n_1, \ldots, n_c)$ and letting $\gamma : [0,1] \to \mathcal{R}_{>0}^{3+c}$, such that if $n_i(t) = pr_{3+i}(t)$, for $0 \leq i \leq c$, then;*

$\frac{n_i'}{\nu_i} = \frac{n_j'}{\nu_j}$, *for* $1 \leq i < j \leq c$

where $\{\nu_1, \ldots, \nu_c\}$ are the stoichiometric coefficients. If $n(t) = \sum_{i=0}^{c} n_i(t)$, and $x_i(t) = a_i(t) = \frac{n_i}{n}(t)$, $0 \leq i \leq c$, then $Q(pr_{12}(t)) = \prod_{i=1}^{p} a_i(t)^{\nu_i}$ and $n_0 > 0$ is a fixed constant. Note that $n > 0$ and the x_i are well defined, $0 \leq i \leq c$. The existence of feasible paths follows easily from the proof of Lemma 2.19, where we are free to take any $n_0 > 0$.

Lemma 10.2. *In the case of dilute solutions, with no interaction of the solvent, a feasible path γ is a dynamic equilibrium path iff $pr(\gamma_{12}) \subset C_f$, for some $f \in \mathcal{R}_{>0}$ iff $\frac{dW}{dt} = 0$.*

Proof. We have that;

$W = \prod_{i=1}^{c} a_i^{\nu_i} = \prod_{i=1}^{c} x_i^{\nu_i}$

$= W = f \ (*)$

If γ is a feasible path, then $pr_{12}(\gamma) \subset W_{>0}$, otherwise, we could find (T, P), with $x_i(T, P) \leq 0$, contradicting the fact that $n_i > 0$, $n > 0$. It follows that $f > 0$. With $f > 0$, follow through the proof of Lemma 2.17, replacing β with $\sum_{i=0}^{c} d_i$, where $d_0 = n_0$. Clearly $n_0' = 0$ so we obtain the first direction. The rest of the proof follows from Lemma 2.20, using the additional fact that $n_0' = 0$.

□

Lemma 10.3. *In the case of dilute solutions, with no interaction of the solvent, and a_0 assumed constant, a feasible path γ is a dynamic equilibrium path iff $pr(\gamma_{12}) \subset C_c$, for some $c \in \mathcal{R}_{>}$, iff $\frac{dQ}{dt} = 0$.*

Proof. We have that;

$\prod_{i=1}^{c} a_i^{\nu_i} = \frac{Q}{a_0}$

$= \prod_{i=1}^{c} x_i^{\nu_i}$

$= \frac{c}{a_0} = d$

If γ is a feasible path, then $pr_{12}(\gamma) \subset Q_{>0}$, otherwise, we could find (T, P), with $x_i(T, P) \leq 0$, contradicting the fact that $n_i > 0$, for $0 \leq i \leq c$, $n > 0$. It follows that $c > 0$, $d > 0$. With $d > 0$, follow through the proof of Lemma 2.17 again, getting the other directions from Lemma 2.20.

□

Lemma 10.4. *In the case of dilute solutions, with no interaction of the solvent, a feasible path γ is a dynamic equilibrium path iff $pr(\gamma_{12}) \subset C_f$, for some $f \in \mathcal{R}_{>0}$ iff $\frac{dQ}{dt} = 0$.*

Proof. With the same caveat as in Lemma 10.3, we have that;

$a_0 \prod_{i=1}^{c} a_i^{\nu_i} = x_0 \prod_{i=1}^{c} x_i^{\nu_i}$

$= \prod_{i=0}^{c} x_i^{\mu_i}$

$= Q = f \ (*)$

where $x_i = \frac{n_i}{n}$, $\mu_0 = 1$, $\mu_i = \nu_i$, $1 \leq i \leq c$.

Using the relation $(*)$, differentiating and using the facts that, for $1 \leq i \leq c - 1$;

$n_i' = \frac{\mu_i n_c'}{\mu_c}$, $n_i = \frac{\mu_i n_c}{\mu_c} + d_i$, $n_0' = 0$, $n_0 = d_0$

we obtain that;

$(\prod_{i=0}^{c} x_i^{\mu_i})' = \sum_{i=0}^{c} \mu_i x_i^{\mu_i - 1} x_i' \prod_{j \neq i} x_j^{\mu_j}$

$= f \sum_{i=0}^{c} \mu_i x_i^{\mu_i - 1} x_i' x_i^{-\mu_i}$

$= f \sum_{i=0}^{c} \mu_i x_i^{-1} x_i'$

$= 0$

so that;

$= \sum_{i=0}^{c} \mu_i \frac{n}{n_i} \frac{(n_i' n - n_i n')}{n^2}$

$= \sum_{i=0}^{c} \mu_i (\frac{n_i'}{n_i} - \frac{n'}{n})$

$= \sum_{i=1}^{c-1} \frac{\mu_i^2 n_c'}{\nu_i n_c + \mu_c d_i} + \frac{\mu_c n_c'}{n_c} - \lambda(\frac{\sum_{i=0}^{c} n_i'}{\sum_{i=0}^{c} n_i})$

$= \sum_{i=1}^{c-1} \frac{\mu_i^2 n_c'}{\mu_i n_c + \mu_c d_i} + \frac{\mu_c n_c'}{n_c} - \lambda(\frac{(\sum_{i=1}^{c-1} \frac{\mu_i}{\mu_c} + 1) n_c'}{(\sum_{i=1}^{c-1} \frac{\nu_i}{\nu_c} + 1) n_c + \sum_{i=0}^{c-1} d_i})$

$= 0$ (B)

where $\lambda = \sum_{i=0}^{c} \mu_i = 1 + \sum_{i=1}^{c} \nu_i$

Following the proof of Lemma 2.17, replacing β with $\sum_{i=0}^{c-1} d_i$, we have, if $\sum_{i=1}^{c-1} \mu_i = \sum_{i=1}^{c-1} \nu_i \neq 0$ and $\lambda = 1 + \sum_{i=1}^{c} \mu_i = 1 + \sum_{i=1}^{c} \nu_i \neq 0$, then $n_i' = 0$, for $1 \leq i \leq c$, and clearly we have that $n_0' = 0$. Similarly, if $\lambda = \sum_{i=0}^{c} \mu_i = 1 + \sum_{i=1}^{c} \nu_i = 0$, we obtain the relation;

$\prod_{i=0}^{c} n_i^{\mu_i} = f$

Again, following the proof of Lemma 2.17, if $n_c' \neq 0$, we obtain the relation;

$\sum_{i=1}^{c-1} \frac{\mu_i^2}{\mu_i n_c + \mu_c d_i} + \frac{\mu_c}{n_c} = \sum_{i=1}^{c-1} \frac{\nu_i^2}{\nu_i n_c + \nu_c d_i} + \frac{\nu_c}{n_c}$

$= 0$

and, by the proof there, we obtain that $n_i' = 0$, for $1 \leq i \leq c$. As $n_0' = 0$, we obtain the result. We are left with the case $\sum_{i=1}^{c-1} \mu_i = \sum_{i=1}^{c-1} \nu_i = 0$. As in the proof of Lemma 2.17, we can assume this choosing the appropriate pivot. The other directions in the Lemma follow from a simple modification of Lemma 2.20.

□

Lemma 10.5. *In Lemmas 2.7 to 2.15, for the standard cell, and considering a dilute solution with no interaction of the solvent, replacing Q defined as $\prod_{i=1}^{c} a_i^{\nu_i}$ by the same definition of W;*

If we assume without approximation that $\mu_i = \mu_i^\circ + RTln(a_i)$, $1 \leq i \leq c$, then;

the same results as Lemma 5.2, setting $a_0(T, P) = 1$, with the caveat that in the final claim $W = 1$ and any path is a dynamical equilibrium line.

Proof. The proof is clear. □

Lemma 10.6. *In Lemmas 2.7 to 2.15, for the standard cell, and considering a dilute solution with no interaction of the solvent, replacing Q defined as $\prod_{i=1}^{c} a_i^{\nu_i}$ by;*

$a_0(\prod_{i=1}^{c} a_i^{\nu_i}) = x_0(\prod_{i=1}^{c} a_i^{\nu_i})$

If we assume without approximation that $\mu_i = \mu_i^\circ + RTln(a_i)$, $0 \leq i \leq c$, then;

the same results as Lemma 5.2, with the new definition of $a_0(T, P) = x_0(T, P)$.

Proof. The proof is clear. □

We reformulate Lemmas 3.2 to 3.6 in this context, assuming Henry's law for the solutes and the solvent an ideal solution;

Lemma 10.7. *In the dilute solution case, with no interaction of the solvent, for the energy function G involving $c + 1$ uncharged species, including the solvent;*

$(\frac{\partial G}{\partial \xi})_{T,P} = \Delta G^\circ + RTln(W) + \epsilon$

where $\epsilon(T, P) = \sum_{i=1}^{c} \nu_i \kappa_i(T) \simeq 0$ and $\kappa_i(T) \simeq 0$ are the error terms for the i'th uncharged species in Definition 6.1, $1 \leq i \leq c$.

Proof. The proof is clear from Lemma 3.2 and the fact that, as $dn_0 = 0$;

$dG = \sum_{i=0}^{c} \mu_i dn_i = \sum_{i=1}^{c} \mu_i dn_i$

so that $(\frac{\partial G}{\partial \xi})_{T,P} = \sum_{i=1}^{c} \nu_i \mu_i$ and $\Delta G^\circ = \sum_{i=1}^{c} \nu_i \mu_i^\circ$.

□

Lemma 10.8. *For a dilute solution, with no interaction of the solvent, we have, using the definition of* $\epsilon(T) = \sum_{i=1}^{c} \nu_i \kappa_i(T)$*, where the error terms* $\kappa_i(T)$*,* $1 \leq i \leq c$ *occur in Definition 6.1, that the same results as Lemma 3.3 hold, replacing* $\epsilon(P)$ *with* $\epsilon(T)$ *and* δ *with* $\epsilon(T) = \sum_{i=1}^{c} \nu_i \kappa_i(T)$ *again, and using* W *instead of* Q*.*

Proof. The proof is clear from the proof of Lemma 3.3, using the observation from Lemma 10.7.

□

Lemma 10.9. *For a dilute solution, with no interaction of the solvent, we have the same result as Lemma 3.4 hold, replacing* $\epsilon(P(T))$ *by* $\epsilon(T)$ *along the quasi-chemical equilibrium lines, and using* W *instead of* Q*.*

Proof. The proof is again clear from the proof of Lemma 3.4.

□

Lemma 10.10. *For a dilute solution, with no interaction of the solvent, we have the same results as Lemma 3.5 hold, replacing* $\epsilon(P')$ *by* $\epsilon(T_1)$*. In particularly, if* $\epsilon \neq 0$*, we have that;*

$W(T,P) = e^{\frac{\epsilon(P-P^\circ)-\epsilon(T)}{RT}}$

and, if $\epsilon = 0$*, we have that;*

$W(T,P) = e^{\frac{-\epsilon(T)}{RT}}$

Proof. The proof is clear from the proof of Lemma 3.5.

□

Lemma 10.11. *For a dilute solution, with no interaction of the solvent, we have that, if* $\epsilon \neq 0$*;*

$grad(W)(T,P) = ((\frac{-\epsilon(P-P^\circ)}{RT^2} + \frac{\epsilon(T)}{RT^2} - \frac{\frac{d\epsilon}{dT}(T)}{RT})e^{\frac{\epsilon(P-P^\circ)-\epsilon(T)}{RT}},$

$(\frac{\epsilon}{RT})e^{\frac{\epsilon(P-P^\circ)-\epsilon(T)}{RT}})$

and, if $\epsilon = 0$*;*

$$grad(W)(T,P) = ((\frac{\epsilon(T)}{RT^2} - \frac{\frac{d\epsilon}{dT}(T)}{RT})e^{\frac{-\epsilon(T)}{RT}}, 0)$$

The paths of maximal reaction in the region $|grad(W)(T,P)| > 1$, $W(T,P) > 0$*, are given by implicit solutions to the differential equations;*

$$\frac{dP}{dT} = \frac{\epsilon T}{(-\epsilon(P-P^\circ)+\epsilon(T)-T\frac{d\epsilon}{dT}(T))}$$

$$\frac{dP}{dT} = 0$$

respectively.

Proof. The computation follows easily from the proof of Lemma 6.7, replacing $\epsilon(P,T)$ by $\epsilon(T)$. We also note that in the proof of maximal reaction, see Lemma 3.6, we have to change β to $\sum_{i=0}^{c+1} n_{i,0}$, where $n_{i,0}$ is the fixed molar amount of the solvent. This effects α_1 but we still have that $\alpha_1 \neq 0$ and the rest of the proof is unchanged.

□

Remarks 10.12. *We can also formulate versions of Lemmas 10.7 to 10.11 for the activity coefficient* Q *instead of* W*, mentioned in the introduction to this section 10. However, although the proof should go through, it is more difficult, and left as an exercise for the reader, combining the methods of Sections 3 and 5. However, it seems unnecessary when we can derive the main results with the coefficient* W*.*

11. Dilute solutions with Fugacity and No Solvent Interaction

Again, we can define activity coefficients either by $W = \prod_{i=1}^{c} b_i^{\nu_i}$, or the more conventional $Z = b_0 \prod_{i=1}^{c} b_i^{\nu_i}$ where;

$$b_0 = x_0$$

$$b_i = x_i,\ 1 \leq i \leq c$$

See the introductions to Section 8 and Section 10 with the Remark 10.1. We will again consider both cases.

Lemma 11.1. *In the case of dilute solutions, with no interaction of the solvent, a feasible path γ is a dynamic equilibrium path iff $pr(\gamma_{12}) \subset C_f$, for some $f \in \mathcal{R}_{>0}$ iff $\frac{dW}{dt} = 0$.*

Proof. Copy the proof of Lemma 10.2. □

Lemma 11.2. *In the case of dilute solutions, with no interaction of the solvent, and b_0 assumed constant, a feasible path γ is a dynamic equilibrium path iff $pr(\gamma_{12}) \subset C_f$, for some $f \in \mathcal{R}_{>0}$ iff $\frac{dZ}{dt} = 0$.*

Proof. We have that;

$\prod_{i=1}^{c} b_i^{\nu_i} = \frac{Z}{b_0}$

$= \prod_{i=1}^{c} x_i^{\nu_i}$

$= \frac{f}{b_0} = d$

Now copy the proof of Lemma 10.3.

□

Lemma 11.3. *In the case of dilute solutions, with no interaction of the solvent, a feasible path γ is a dynamic equilibrium path iff $pr(\gamma_{12}) \subset C_f$, for some $f \in \mathcal{R}_{>0}$ iff $\frac{dZ}{dt} = 0$.*

Proof. We have that;

$b_0 \prod_{i=1}^{c} b_i^{\nu_i} = x_0 \prod_{i=1}^{c} x_i^{\nu_i}$

$= Z = f$

Now copy the proof of Lemma 10.4.

□

Lemma 11.4. *In Lemmas 2.7 to 2.15, for the standard cell, and considering a dilute solution with no interaction of the solvent, replacing Q defined as $\prod_{i=1}^{c} a_i^{\nu_i}$ by the same definition of W;*

If we assume without approximation that $\mu_i = \mu_i^{\circ} + RTln(b_i)$, $1 \leq i \leq c$, then;

the same results as Lemma 5.2, setting $a_0(T, P) = 1$, with the same caveat as Lemma 10.5.

Proof. The proof is clear, as in Lemma 10.5.

□

Lemma 11.5. *In Lemmas 2.7 to 2.15, for the standard cell, and considering a dilute solution with no interaction of the solvent, replacing Q defined as $\prod_{i=1}^{c} a_i^{\nu_i}$ by;*

$Z = b_0(\prod_{i=1}^{c} b_i^{\nu_i}) = x_0(\prod_{i=1}^{c} b_i^{\nu_i})$

If we assume without approximation that $\mu_i = \mu_i^\circ + RTln(b_i)$, $0 \leq i \leq c$, then;

the same results as Lemma 5.2, with the new definition of $b_0(T,P) = x_0(T,P)$ replacing $a_0(T,P)$ in the Lemma.

Proof. The proof is clear, as in Lemma 10.6.

□

We reformulate Lemmas 3.2 to 3.6 in this context, assuming the approximation to Henry's law for the solutes and the approximation to Raoult's law for the solvent;

Lemma 11.6. *In the dilute solution case, with no interaction of the solvent, for the energy function G involving $c+1$ uncharged species;*

$(\frac{\partial G}{\partial \xi})_{T,P} = \Delta G^\circ + RTln(W) + \epsilon(T,P)$

where $\epsilon(T,P) = \sum_{i=1}^{c} \nu_i \psi_i(T,P)$, and ψ_i, for $1 \leq i \leq c$ are the error terms for the solutes in Definition 8.1.

Proof. The proof is clear from Lemma 3.2, with the same observation as in Lemma 10.7.

□

Lemma 11.7. *For a dilute solution, with no interaction of the solvent, we have, using the definition of $\epsilon(T,P)$ in Lemma 11.6, the error terms $\psi_i(T,P)$, $1 \leq i \leq c$ in Definition 8.1, that the same results as Lemma 3.3 hold, replacing $\epsilon(P)$ with $\epsilon(T,P)$ and δ with $\epsilon(T,P^\circ) = \sum_{i=1}^{c} \nu_i \psi_i(T,P^\circ)$, using W instead of Q.*

Proof. The proof is clear from the proof of Lemma 3.3, using Lemma 11.6.

□

Lemma 11.8. *For a dilute solution, with no interaction of the solvent, we have the same results as Lemma 3.4 hold, replacing $\epsilon(P(T))$ by $\epsilon(T, P(T))$ along the quasi-chemical equilibrium lines.*

Proof. The proof is again clear from the proof of Lemma 3.4 and Lemma 11.7.

□

Lemma 11.9. *For a dilute solution, with no interaction of the solvent, we have the same results as Lemma 3.5 hold, replacing $\epsilon(P')$ by $\epsilon(T_1, P')$. In particularly, if $\epsilon \neq 0$, we have that;*

$$W(T,P) = e^{\frac{\epsilon(P-P^{\circ})-\epsilon(T,P)}{RT}}$$

and, if $\epsilon = 0$, we have that;

$$W(T,P) = e^{\frac{-\epsilon(T,P)}{RT}}$$

Proof. The proof is again clear from the proof of Lemma 3.5 and Lemma 11.8.

□

Lemma 11.10. *For a dilute solution, with no interaction of the solvent, we have that, if $\epsilon \neq 0$;*

$$grad(W)(T,P) = ((\frac{-\epsilon(P-P^{\circ})}{RT^2} + \frac{\epsilon(T,P)}{RT^2} - \frac{\frac{\partial \epsilon}{\partial T}(T,P)}{RT})e^{\frac{\epsilon(P-P^{\circ})-\epsilon(T,P)}{RT}},$$

$$(\frac{\epsilon}{RT} - \frac{\frac{\partial \epsilon}{\partial P}(T,P)}{RT})e^{\frac{\epsilon(P-P^{\circ})-\epsilon(T,P)}{RT}})$$

and, if $\epsilon = 0$;

$$grad(Z)(W,P) = ((\frac{\epsilon(T,P)}{RT^2} - \frac{\frac{\partial \epsilon}{\partial T}(T,P)}{RT})e^{\frac{-\epsilon(T,P)}{RT}}, \frac{-\frac{\partial \epsilon}{\partial P}(T,P)}{RT}e^{\frac{-\epsilon(T,P)}{RT}})$$

The paths of maximal reaction in the region $|gradW(T,P)| > 1$, $W(T,P) > 0$, are given by implicit solutions to the differential equations;

$$\frac{dP}{dT} = \frac{\epsilon T - T\frac{\partial \epsilon}{\partial P}(T,P)}{(-\epsilon(P-P^{\circ})+\epsilon(T,P)-T\frac{\partial \epsilon}{\partial T}(T,P))}$$

$$\frac{dP}{dT} = \frac{-T\frac{\partial \epsilon}{\partial P}(T,P)}{\epsilon(T,P)-T\frac{\partial \epsilon}{\partial T}(T,P)}$$

respectively.

Proof. The proof is the same as Lemma 6.7, using W instead of Z, noting that the error term $\epsilon(T, P)$ depends on P, unlike Lemma 10.11.

□

Remarks 11.11. *Again we can formulate Lemmas 11.6 to 11.10 using Q instead of W, see Remark 10.12. The results of the section might be useful in the production of ethanol, using H_2O as the solvent, by varying the temperature and pressure of the reaction, $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$, see* [7] *as well.*

12. Electrochemistry with Error Terms, Fugacity and No Interaction of the Solvent

Using the new error term $\epsilon(T, P)$ and the activity coefficient W from Section 11, we have that;

Lemma 12.1. *The Nernst Equation for the Standard Cell*

At electrical chemical equilibrium (T, P) and (T, P°) for the standard cell;

$$(E - E^\circ)(T, P) = -\frac{RTln(W(T,P))}{2F} - \frac{\epsilon(T,P)}{2F}$$

Proof. Just use the proof of Lemma 4.1, replacing $\epsilon(P)$ with the error term $\epsilon(T, P)$ from Section 11, noting that for the Gibbs funcion involving $c + 1$ species, including the solvent, $(\frac{\partial G}{\partial \xi})_{T,P} = \sum_{i=1}^{c} \nu_i \mu_i$ again.

□

Lemma 12.2. *At electrical chemical equilibrium (T, P) and (T, P°), and chemical equilibrium (T, P);*

$$\Delta G^\circ = 2F(E - E^0)$$

Proof. Follow the proof of Lemma 4.2, replacing $\epsilon(P)$ with $\epsilon(T, P)$.

□

Lemma 12.3. *If $\epsilon = 0$, we have, for all $T_1 > 0$, that;*

$(\frac{\partial G}{\partial \xi})_{T,P}|_{(T_1,P_1)} = (\frac{\partial G}{\partial \xi})_{T,P}|_{(T_1,P_1^\circ)}$

iff;

$E(T_1, P_1) = E(T_1, P_1^\circ) = E^\circ(T_1)$

where G is the Gibbs energy function for the $c+1$ charged and uncharged species.

Proof. Follow the proof of Lemma 4.3, replacing the result of Lemma 1.5, that $(\frac{\partial G_{chem'}}{\partial \xi})_{T,P}$ is independent of P, with the corresponding result in Lemma 11.9. □

Lemma 12.4. *We have, for all $T_1 > 0, P_1 > 0$, that;*

$2F(E(T_1, P_1) - E^\circ(T_1)) = (\frac{\partial G}{\partial \xi})_{T,P}|_{(T_1,P_1)} - (\frac{\partial G}{\partial \xi})_{T,P}|_{(T_1,P_1^\circ)} - RT_1 ln(Z(T_1, P_1)) - \epsilon(T_1, P_1)$ $(*)$

Proof. Follow the proof of Lemma 4.4, replacing $\epsilon(P)$ with $\epsilon(T, P)$.

□

Remarks 12.5. *The result of Lemma 12.4 combined with the determination of the activity coefficient W in Lemma 11.9 and the error term $\epsilon(T, P)$ in Lemma 11.6 can be used to determine the unknown quantity $(\frac{\partial G}{\partial \xi})_{T,P}$. We can measure the potential difference between the cathode and anode along the dynamical equilibrium paths provided by Lemma 11.9 and then use the formula $(*)$ in Lemma 12.4. Once this is determined, we then alter the power supply, in accordance with $(*)$, to push the reaction along the paths of maximal reaction given in Lemma 11.10. This should improve the efficiency of the production of hydrogen, in the case of the reaction, given by $H_2 + 2AgCl + 2e^-(R) \rightarrow 2HCl + 2Ag + 2e^-(L)$, where we use water H_2O as a solvent with no interaction.*

13. The Constant Change in Enthalpy Assumption

Lemma 13.1. *We can assume that ΔH° is constant.*

Proof. We have, by the definition of enthalpy, the laws of differentials, the first law of thermodynamics, with $dP = 0$, that;

$$dH = dU + PdV + VdP$$

$$= dU + PdV$$

$$= (dQ - PdV) + PdV$$

$$= dQ$$

where Q is the internal energy including work, or heat. From this calculation, as any internal energy change dU and change in volume dV is unaffected by adding a solvent not involved in the reaction, and by re-establishing the pressure of the original reaction, it is clear that $\Delta H^{\circ}(T) = \Delta H^{\circ,solv}(T)$, where $\Delta H^{\circ,solv}(T)$ is calculated by adding a solvent not involved in the reaction at the same pressure P°. As in Kirchoff's Law of Thermodynamics, we have that;

$$\Delta H^{\circ}(T)$$

$$\Delta H^{\circ,solv}(T) = \Delta H^{\circ,solv}(T_0) + \int_{T_0}^{T} \frac{d(\Delta H^{\circ,solv}(T))}{dT} dT$$

$$= \Delta H^{\circ,solv}(T_0) + \int_{T_0}^{T} \frac{d(\Delta Q_{solv}(T))}{dT} dT$$

$$= \Delta H^{\circ,solv}(T_0) + \int_{T_0}^{T} C_{solv}(T) dT$$

$$= \Delta H^{\circ}(T_0) + \int_{T_0}^{T} C_{solv}(T) dT \ (M)$$

where $C_{solv}(T) = \Delta(\frac{dQ_{solv}}{dT})(T)$ is the change in the heat capacity of the mixture, after one mole of reaction. If we confine ourselves to a small temperature range, we can, therefore assume that ΔH° is approximately temperature independent. However, we can also add solvent to the reaction, to lower the magnitude of $C_{solv}(T)$, as the heat capacity before and after the reaction would approach that of the solvent, and extend the temperature range of the reaction. More precisely, we have, by the law of mixtures for heat capacities, the fact that $m_{mix,solv}$ is conserved during 1 mole of reaction, that;

$$C_{solv}(T) = C_{fin,solv}(T) - C_{in,solv}(T)$$

$$= \frac{1}{m_{mix,solv}}(\sum_{i=0}^{c} m_{i,fin}C_{i,fin}(T) - \sum_{i=1}^{c} m_{i,in}C_{i,in}(T))$$

$$= \frac{N_A}{m_{mix,solv}}(\sum_{i=0}^{c} n_{i,fin}m_{i,molec}C_{i,fin}(T) - \sum_{i=0}^{c} n_{i,in}m_{i,molec}C_{i,in}(T))$$

$$= \frac{N_A}{m_{mix,solv}}(\sum_{i=0}^{c} n_{i,fin}m_{i,molec}m_{i,fin}SC_i(T) - \sum_{i=0}^{c} n_{i,in}m_{i,molec}m_{i,in}SC_i(T))$$

$$= \frac{N_A^2}{m_{mix,solv}}(\sum_{i=0}^{c} n_{i,fin}^2m_{i,molec}^2SC_i(T) - \sum_{i=0}^{c} n_{i,in}^2m_{i,molec}^2SC_i(T))$$

$$= \frac{N_A^2}{m_{mix,solv}}(\sum_{i=0}^{c} (n_{i,in}-\nu_i)^2m_{i,molec}^2SC_i(T) - \sum_{i=0}^{c} n_{i,in}^2m_{i,molec}^2SC_i(T))$$

$$= -\frac{2}{m_{mix,solv}}(\sum_{i=1}^{c} \nu_i m_{i,in}m_{i,mol}SC_i(T)) + \frac{1}{m_{mix,solv}}(\sum_{i=1}^{c} \nu_i^2m_{i,mol}^2SC_i(T))$$

$$= \theta(T) + v(T), \ (N)$$

where $\nu_0 = 0$ and ν_i, for $1 \leq i \leq c$ are the stochiometric coefficients for the original reaction, ([7]).

Using the fact that $\frac{m_{i,in}}{m_{mix,solv}} \to 0$, for $1 \leq i \leq c$, by increasing the mass of the solvent not involved in the reaction, we have that $\theta(T) \to 0$, and, similarly, $v(T) \to 0$ as $m_{mix} \to \infty$ with $\{m_{i,in}, m_{i,fin}, m_{i,molec}, m_{i,mol}\}$ denoting the initial, final, molecular and molar masses of substance i respectively, $\{C_i, SC_i, C_{in}, C_{fin}\}$ denoting the heat capacities of substance i, the specific heat capacities of substance i, the initial heat capacity of the mixture and the final heat capacity of the mixture respectively. In particular, we see that, as $m_{mix,solv} \to \infty$, which we can achieve, by increasing the solvent not involved in the reaction, $C_{solv}(T) \to 0$. We then have, by $(M), (N)$, that;

$$\Delta H^{\circ}(T) = \Delta H^{\circ}(T_0) + \int_{T_0}^{T}(\theta(S) + v(S))dS$$

$$= \Delta H^{\circ}(T_0) + w(T_0, T)$$

$$\to \Delta H^{\circ}(T_0)$$

as we can make the convergence uniform on the interval (T_0, T), given that the specific heat capacities $SC_i(S)$ are bounded on (T_0, T),

[7] During the paper, we denoted by substance 0 a solvent either involved or not involved in the reaction. Here, we are relabelling the reaction to include this solvent in the original mixture consisting of substances indexed by $1 \leq i \leq c$. We are assuming that it is possible to add a solvent not involved in the reaction within a certain time range, even though it might be involved within the original mixture.

for $1 \leq i \leq c$.

□

14. Independence of Path and Existence

Lemma 14.1. *For water electrolysis, no substance is formed in a temperature pressure loop. With the assumption that ΔH^{circ} is constant, we have that $\lambda = \Delta H^{\circ} - \epsilon P^{\circ}$. If D_c is a quasi-chemical equilibrium line in the theoretical limit, which we have computed, intersecting $P = P^{\circ}$ at (T_1, P°), and projecting onto an interval (T_1, T_2), with $T_1 < T_2$, then, making $w(T_1, T_2) \simeq 0$, see Section 13, for the mass of the mixture sufficiently large, we have that $\lambda(T_1, T_2) \simeq \Delta H^{\circ, ref}(T_1, T_2) - \epsilon(T_1, T_2)P^{\circ}$, where $\epsilon((T_1, T_2))$ can be effectively determined. There is a thermodynamic argument for no substance formed in a loop, which holds generally. There is a symmetry in the chemical potentials.*

Proof. The first result is clear for water electrolysis by Lemma 3.9. The second claim, with the assumption that ΔH° is constant, follows from the proof of Lemma 2.12, and in later sections, when we introduce error terms. The next claim follows easily as $w(T_1, T_2) \simeq 0$, see Section 13, and the computation of λ without the error term $w(T_1, T_2)$. The computation of $\epsilon(T_1, T_2)$ is given in Lemma 2.12.We take it as reasonable then, that if there are 2 distinct feasible paths between (T_0, P_0) and (T, P), with a given initial condition $(n_{1,0}, \ldots n_{c,0})$ at (T_0, P_0), then the extent of the reaction ξ determined by the paths $\{\gamma_1, \gamma_2\}$ should be the same, $(*)$. If this were not the case, then reversing one of the paths, we could obtain a reaction extent at (T_0, P_0) along a loop γ. For the thermodynamic argument for no substance formed in a loop. Using the slight variation in the volume of liquids along a reaction path, and the fact that we return to the original pressure P_0 in a loop, we would have that;

$$\Delta H = \int_{\gamma} dH$$

$$= \int_{\gamma} d(U + VP)$$

$$= \int_{\gamma} dU + PdV + VdP$$

$$= \int_{\gamma} dU + dL + VdP$$

$= \Delta U + \Delta L + \int_\gamma V dP$

$\simeq \Delta U + \Delta L + V_0 \int_\gamma dP$

$= \Delta U + \Delta L$

$= \Delta Q$

If ΔH is large, this would mean that $\Delta Q \neq 0$, which means that there is a change in heat, contradicting the fact that the temperature T_0 is unchanged. If ΔH is small, with $\Delta H = \int_\gamma V dP$, then, by generic considerations of bond energies, the amount of substance ξ formed by the reaction would also be quite small. For the last claim, if $(*)$ holds for a single pair $\{A, B\}$, then it holds for all pairs $\{C, D\}$, as we can compose with reactions from A to C and D to B. If follows that if we define;

$f_i(T, P) = e^{\frac{\mu_i(T,P) - \mu_i^\circ(T)}{RT}} > 0$, for $1 \leq i \leq c$

so that $f_i(T, P) = x_i(T, P) = \frac{n_i(T,P)}{n(T,P)}$, then, by the definition of extent;

$\xi = \frac{n_i - n_{i,0}}{\nu_i}$

$n_i = \nu_i \xi + n_{i,0}$ $(1 \leq i \leq c)$

we must have that;

$x_i = \frac{n_i}{n} = \frac{\nu_i \xi + n_{i,0}}{\sum_{i=1}^c (\nu_i \xi + n_{i,0})} = \frac{\nu_i \xi + n_{i,0}}{\lambda \xi + n_0} = f_i$ $(1 \leq i \leq c)$

where $\lambda = \sum_{i=1}^c \nu_i$, so that;

$\nu_i \xi + n_{i,0} = (\lambda \xi + n_0) f_i$

$\xi = \frac{n_{i,0} - n_0 f_i}{\kappa f_i - \nu_i}$, $(1 \leq i \leq c)$

so that, for $1 \leq i \leq j \leq c$;

$\frac{n_{i,0} - n_0 f_i}{\lambda f_i - \nu_i} = \frac{n_{j,0} - n_0 f_j}{\lambda f_j - \nu_j} = \xi$ $(**)$

As all the steps are reversible, the requirement $(**)$ at (T, P), for all $(n_{1,0}, \ldots, n_{c,0})$ satisfying $\frac{n_{i,0}}{n_0} = f_i(T_0, P_0)$, (so that $\xi(T_0, P_0) = 0$, $(***)$), is equivalent to $(*)$. We impose the condition that $Ker(M) \cap \mathcal{R}^c_{>0} \neq \emptyset$, where;

$M_{ii} = f_i(T_0, P_0) - 1$, $(1 \leq i \leq c)$

$M_{ij} = f_i(T_0, P_0)$ $(1 \leq i \leq c, 1 \leq j \leq c, i \neq j)$

so that there exists at least one choice $(n_{1,0}, \ldots, n_{c,0}) \in \mathcal{R}^c_{>0}$ satisfying $(***)$. With this requirement there do exist feasible paths between any 2 pairs (A, B), see Lemma 2.19. If not, there is no feasible path involving a reaction from $A = (T_0, P_0)$, which seems physically unreasonable. We can then, using $(***)$, rewrite $(**)$ as;

$\frac{\frac{n_{i,0}}{n_0} - f_i}{\lambda f_i - \nu_i} = \frac{\frac{n_{j,0}}{n_0} - f_j}{\lambda f_j - \nu_j}$, $(1 \leq i \leq j \leq c)$

iff $\frac{f_i(T_0,P_0) - f_i(T,P)}{\lambda f_i(T,P) - \nu_i} = \frac{f_j(T_0,P_0) - f_j(T,P)}{\lambda f_j(T,P) - \nu_j}$

so that, reversing (T, P) and (T_0, P_0);

iff $\frac{f_i(T,P) - f_i(T_0,P_0)}{\lambda f_i(T_0,P_0) - \nu_i} = \frac{f_j(T,P) - f_j(T_0,P_0)}{\lambda f_j(T_0,P_0) - \nu_j}$

iff $\frac{\lambda f_j(T,P) - \nu_j}{\lambda f_i(T,P) - \nu_i} = \frac{f_j(T_0,P_0) - f_j(T,P)}{f_i(T_0,P_0) - f_i(T,P)}$

$= \frac{f_j(T,P) - f_j(T_0,P_0)}{f_i(T,P) - f_i(T_0,P_0)}$

$= \frac{\lambda f_j(T_0,P_0) - \nu_j}{\lambda f_i(T_0,P_0) - \nu_i}$

iff $\frac{\lambda f_j(T,P) - \nu_j}{\lambda f_j(T_0,P_0) - \nu_j} = \frac{\lambda f_i(T,P) - \nu_i}{\lambda f_i(T_0,P_0) - \nu_i}$

The same arguments apply when we incorporate error terms into the functions $\{f_i : 1 \leq i \leq p\}$ or extend the functions to a set $\{f_i : 0 \leq i \leq p\}$, when we consider a solvent, which we do in later sections.

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