Open Journal of
Mathematical Sciences

PSR Press

Article

Equilibria in electrochemistry and maximal rates of reaction

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Academic Editor: Merve Ilkhan Kara
Received: Received: 20 April 2022; Accepted: 1 January 2023; Published: 31 March 2023.

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.

Keywords: Gibbs' definition of chemical equilibrium; Activity coefficient; Electrochemistry; Nernst equation; Maximal reaction paths.

MSC: 35Q40; 35Q60; 83A05.

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1. Introduction

This paper is divided into 12 sections. In §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 idealized law in the behavior 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 6, 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 7, we use an entropy calculation to find $(\frac{\partial G}{\partial \xi})_{T,P}$ and combine the result with Lemma 6 to calculate the activity coefficient Q. In Lemma 11, 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 generalized 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 12 and again later generalized.

In §3, we consider ideal solutions and introduce a fixed error term from Raoult's law. The results from §2 generalize and in Lemma 19, we find the paths of maximal reaction, in the sense of maximizing extent ξ, implicitly, in terms of temperature and pressure (T, P). We apply the results to electrochemistry in §4. In §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 24. In §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, and obtaining the maximal reaction paths in Lemma 31.

In §7, we introduce new fixed error terms from fugacity, in Definition 7. We alter the conventional definition of Q to incorporate fugacity in the error term and obtain the paths of maximal reaction in Lemma 37. We apply the results to electrochemistry in §8, in particular the reaction in catalyzers, and give a strategy for improving the efficiency of hydrogen and oxygen production from water in Remarks 8. In §9, we consider the case when there is no interaction of the solvent, and in §9 and §10, 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 §5. We suggest the results here could be used in maximizing ethanol production. We gain apply the results to electrochemistry in §11, in particularly the standard cell.

In §12, 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 §13, we consider independence and existence of paths.

2. The idealized case

Definition 1. For c substances, we define the Gibbs energy $G(T,P,n_1,\ldots,n_c)$ 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 $H(T,P,n_1,\ldots,n_c)$ by;

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

see [7] and [5]. We define the Gibbs energy at standard pressure $G^\circ(T,n_1,\ldots,n_c) = G(T,P^\circ,n_1,\ldots,n_c)$, 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;

$$\begin{aligned} a_1 &= \gamma_1 x_1 \simeq 1, \\ a_i &= \frac{\gamma_i m_i}{m^\circ}, \qquad\qquad (2 \leq i \leq c), \end{aligned}$$

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 [7], 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 $\gamma : [0,1] \rightarrow (T,P,n_1,\ldots,n_c)$, 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.

Lemma 1. *Let G be the Gibbs energy, please explain other variables, then we have*

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

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

$$\begin{aligned} dG &= \frac{\partial G}{\partial T}_{P,n} dT + \frac{\partial G}{\partial P}_{T,n} dP + \sum_{i=1}^{c} \frac{\partial G}{\partial n_i}_{T,P,n'} dn_i \\ &= \frac{\partial G}{\partial T}_{P,n} dT + \frac{\partial G}{\partial P}_{T,n} dP + \sum_{i=1}^{c} \mu_i dn_i. \end{aligned} \tag{1}$$

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 (1), we have that;

$$\begin{aligned} dU &= TdS - PdV, \\ dG &= dU + VdP + PdV - SdT - TdS \\ &= (TdS - PdV) + VdP + PdV - SdT - TdS \\ &= -SdT + VdP \\ &= \frac{\partial G}{\partial T}_{P,n} dT + \frac{\partial G}{\partial P}_{T,n} dP, \end{aligned} \tag{2}$$

so that, from (2), and equating coefficients, $\frac{\partial G}{\partial T}_{P,n} = -S$, $\frac{\partial G}{\partial P}_{T,n} = V$. Substituting into (1), we obtain that;

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

□

Definition 2. The electrical chemical equilibrium is defined by $(\frac{\partial G}{\partial \xi})_{T,P} = 0$, where G is the Gibbs energy function for a charged and uncharged species.

Lemma 2 (The Nernst equation for the standard cell [7])**.** *At electrical chemical equilibrium* (T, P) *and* (T, P°)*, we have*

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

Proof. For c substances with c' the number of the charged species, using Definition 1, we have that the electrostatic potential energy;

$$U_{el} = \sum_{i=1}^{c'} \phi(\overline{x}_i) q_i,$$

where $q_i = N_i e z_i = N_A n_i e z_i$, $\{\overline{x}_i : 1 \leq i \leq c'\}$ 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;

$$\begin{aligned} G(T, P, n_1, \ldots, n_c) &= U + PV - TS \\ &= U_{chem} + U_{el} + PV - TS \\ &= U_{el} + G_{chem} \\ &= \sum_{j=1}^{c} \phi(\overline{x}_j) q_j + G_{chem} \\ &= \sum_{j=1}^{c} \phi(\overline{x}_j) N_A n_j e z_j + G_{chem}, \end{aligned}$$

so that;

$$
\begin{aligned}
\mu_i &= (\frac{\partial G}{\partial n_i})_{T,P} \\
&= (\frac{\partial(\sum_{j=1}^{c}\phi(\overline{x}_j)N_A n_j e z_j + G_{chem})}{\partial n_i})_{T,P} \\
&= \mu_{i,chem}, \qquad (c'+1 \leq i \leq c) \\
&= \mu_{i,chem} + \frac{\partial(\phi(\overline{x}_i)N_A n_i e z_i)}{\partial n_i}, \quad (1 \leq i \leq c') \\
&= \mu_{i,chem} + \phi(\overline{x}_i)N_A e z_i \\
&= \mu_{i,chem} + \phi(\overline{x}_i)F z_i. \qquad (3)
\end{aligned}
$$

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 5, generalized to a collection involving charged species, using (3), we have that;

$$
\begin{aligned}
(\frac{\partial G}{\partial \xi})_{T,P} &= \sum_{i=1}^{c}\nu_i\mu_i \\
&= 2\mu(HCl) + 2\mu(Ag) - \mu(H_2) - 2\mu(AgCl) + 2\mu(e^-(L)) - 2\mu(e^-(R)) \\
&= (\frac{\partial G_{chem'}}{\partial \xi})_{T,P} + 2\mu(e^-(L)) - 2\mu(e^-(R)) \\
&= (\frac{\partial G_{chem'}}{\partial \xi})_{T,P} + ((2\mu_{chem}(e^-(L)) - 2F\phi(L)) - (2\mu_{chem}(e^-(L)) - 2F\phi(R))) \\
&= (\frac{\partial G_{chem'}}{\partial \xi})_{T,P} + 2F(\phi(R) - \phi(L)) \\
&= (\frac{\partial G_{chem'}}{\partial \xi})_{T,P} + 2EF = 0, \qquad (4)
\end{aligned}
$$

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

$$
\begin{aligned}
(\frac{\partial G_{chem'}}{\partial \xi})_{T,P^\circ} &= \sum_{i=c'+1}^{c}\nu_i\mu_i^\circ \\
&= (\Delta G^\circ_{chem'} + RTln(Q_{chem'}(T,P^\circ))) \\
&= \Delta G^\circ_{chem'}, \qquad (5)
\end{aligned}
$$

using the definition of $Q_{chem'}$ in Definition 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 (4),(5), we obtain;

$$
\begin{aligned}
2E^\circ F &= -(\frac{\partial G_{chem'}}{\partial \xi})_{T,P^\circ} \\
&= -\Delta G^\circ_{chem'}. \qquad (6)
\end{aligned}
$$

Similarly, we have that;

$$
(\frac{\partial G_{chem'}}{\partial \xi})_{T,P} = \sum_{i=c'+1}^{c}\nu_i\mu_i = (\Delta G^\circ_{chem'} + RTln(Q_{chem'}(T,P))), \qquad (7)
$$

so from (4),(7), we obtain that;

$$
\begin{aligned}
2EF &= -(\frac{\partial G_{chem'}}{\partial \xi})_{T,P} \\
&= -(\Delta G^\circ_{chem'} + RTln(Q_{chem'}(T,P))). \qquad (8)
\end{aligned}
$$

Combining (8), (6), we obtain that;

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

so that;

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

☐

Lemma 3. [7] *For the energy function G involving only an uncharged species;*

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

Proof. By Lemma 5, we have that;

$$\begin{aligned} (\frac{\partial G}{\partial \xi})_{T,P} &= \sum_{i=1}^{c} \nu_i \mu_i \\ \Delta G^{\circ} &= \sum_{i=1}^{c} \nu_i \mu_i^{\circ}. \end{aligned} \tag{9}$$

Using (9), the fact that $\mu_i = \mu_i^{\circ} + RTln(a_i)$, and Definition 1, we have that;

$$\begin{aligned} (\frac{\partial G}{\partial \xi})_{T,P} - \Delta G^{\circ} &= \sum_{i=1}^{c} \nu_i(\mu_i - \mu_i^{\circ}) \\ &= \sum_{i=1}^{c} \nu_i(\mu_i^{\circ} + RTln(a_i) - \mu_i^{\circ}) \\ &= \sum_{i=1}^{c} \nu_i RTln(a_i) \\ &= RTln(\prod_{i=1}^{c} a_i^{\nu_i}) = RTln(Q). \end{aligned}$$

☐

Lemma 4. *At electrical chemical equilibrium (T,P) and (T,P°), and chemical equilibrium (T,P), we have*

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

Proof. By Lemma 2, we have that

$$E - E^{\circ} = -\frac{RTln(Q)}{2F}, \tag{10}$$

and, by Lemma 3, we have that

$$0 = (\frac{\partial G}{\partial \xi})_{T,P} = \Delta G^{\circ} + RTln(Q). \tag{11}$$

Rearranging (10) and (11), we obtain the result. ☐

Lemma 5. *Let us take*

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

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

- *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), *we have* $Q(T,P) = 1$ *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* $Q(T,P) = e^{\frac{-\Delta G^\circ}{RT}}$ *and we always have that* $Q(T,P^\circ) = 1$.

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

$$dn_i = \nu_i d\xi, \qquad (1 \leq i \leq c). \tag{12}$$

By Lemma 1, fixing T and P, and using (12), we have

$$dG = \sum_{i=1}^{c} \mu_i dn_i = (\sum_{i=1}^{c} \mu_i \nu_i) d\xi, \tag{13}$$

so that;

$$(\frac{\partial G}{\partial \xi})_{T,P} = \sum_{i=1}^{c} \mu_i \nu_i. \tag{14}$$

The second claim from the first, as

$$\begin{aligned} \Delta G^\circ(T) &= \int_0^1 (\frac{\partial G}{\partial \xi})_{T,P^\circ} \\ &= \int_0^1 (\sum_{i=1}^{c} \nu_i \mu_i^\circ(T)) d\xi \\ &= \sum_{i=1}^{c} \nu_i \mu_i^\circ(T) \int_0^1 d\xi \\ &= \sum_{i=1}^{c} \nu_i \mu_i^\circ(T). \end{aligned}$$

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 (13) and (14), we have

$$dG = (\frac{\partial G}{\partial \xi})_{T,P} = 0, \qquad \text{(independently of } \xi). \tag{15}$$

At chemical equilibrium T, P°, using the first and second claims, and (15), we have

$$dG = (\frac{\partial G}{\partial \xi})_{T,P^\circ} = \sum_{i=1}^{c} \nu_i \mu_i^\circ = \Delta G^\circ = 0.$$

For the second to last claim, and the first direction, we have, by Lemma 3, that $RTln(Q) = 0$, so that $Q = 1$, and, by Lemma 2, that $E - E^\circ = -\frac{RTln(Q)}{2F} = 0$. For the converse, we have by Lemma 3, 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

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

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

For the penultimate claim, in one direction, use Lemma 3, together with the fact that $(\frac{\partial G}{\partial \xi})_{T,P} = 0$ and rearrange, the converse is also clear, by 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 1. □

Lemma 6 (van't Hoff,Gibbs-Helmholtz [7]). *Along a chemical equilibrium path, we have*

$$\begin{aligned} ln(\frac{Q(T_2)}{Q(T_1)}) &= \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^\circ}{T^2} dT \\ \frac{\Delta G^\circ(T_2)}{T_2} - \frac{\Delta G^\circ(T_1)}{T_1} &= -\int_{T_1}^{T_2} \frac{\Delta H^\circ}{T^2} dT. \end{aligned}$$

In particularly, if ΔH° is temperature independent;

$$\begin{aligned} ln(\frac{Q(T_2)}{Q(T_1)}) &= -\frac{\Delta H^\circ}{R}(\frac{1}{T_2} - \frac{1}{T_1}) \\ \frac{\Delta G^\circ(T_2)}{T_2} - \frac{\Delta G^\circ(T_1)}{T_1} &= \Delta H^\circ(\frac{1}{T_2} - \frac{1}{T_1}) \\ \Delta G^\circ(T_1) &= \frac{T_1}{T_2}\Delta G^\circ(T_2) - (\frac{T_1}{T_2} - 1)\Delta H^\circ. \end{aligned}$$

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

$$\begin{aligned} & Q(T_2, P) = e^{\frac{\Delta G^\circ(T_1) - \Delta G^\circ(T_2)}{RT_2}}, \qquad (16) \\ & c = \Delta G^\circ(T_1), \\ & ln(\frac{Q(T_2)}{Q(T_1)}) = ln(Q(T_2)) = \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^\circ - c}{T^2} dT, \\ & \frac{\Delta G^\circ(T_2) - \Delta G^\circ(T_1)}{T_2} = -\int_{T_1}^{T_2} \frac{\Delta H^\circ - c}{T^2} dT, \end{aligned}$$

and if ΔH° is temperature independent;

$$ln(\frac{Q(T_2)}{Q(T_1)}) = ln(Q(T_2)) = -(\frac{\Delta H^\circ - c}{R})(\frac{1}{T_2} - \frac{1}{T_1}), \qquad (17)$$

$$\frac{\Delta G^\circ(T_2) - \Delta G^\circ(T_1)}{T_2} = (\Delta H^\circ - c)(\frac{1}{T_2} - \frac{1}{T_1}), \qquad (18)$$

$$\Delta G^\circ(T_1) = \frac{T_1}{T_2}\Delta G^\circ(T_2) - \Delta H^\circ(\frac{T_1}{T_2} - 1). \qquad (19)$$

Proof. By Lemma 5, we have

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

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

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

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;

$$\frac{d(\Delta G^\circ)}{dT} = -\sum_{i=1}^{c} \nu_i \overline{S}_i^\circ = -\sum_{i=1}^{c} \nu_i \overline{S}_{m,i}^\circ = -\Delta S^\circ. \tag{20}$$

Using the product rule, (20) and the definition of enthalpy, we have

$$\frac{d}{dT}(\frac{\Delta G^\circ}{T}) = \frac{1}{T}\frac{d(\Delta G^\circ)}{dT} - \frac{1}{T^2}\Delta G^\circ = -\frac{\Delta S^\circ}{T} - \frac{\Delta G^\circ}{T^2} = -\frac{\Delta(ST+G)^\circ}{T^2} = -\frac{\Delta H^\circ}{T^2}. \tag{21}$$

By Lemma 5, 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 (21) 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;

$$\begin{aligned} ln(\frac{Q(T_2)}{Q(T_1)}) &= ln(Q)(T_2) - ln(Q)(T_1) \\ &= \frac{-\Delta G^\circ(T_2)}{RT_2} + \frac{\Delta G^\circ(T_1)}{RT_1} \\ &= \int_{T_1}^{T_2} \frac{dln(Q)}{dT} dT \\ &= \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^\circ}{T^2}. \end{aligned} \tag{22}$$

So that, rearranging, we obtain the first claim. Using the fact, by Lemma 3, that;

$$\begin{aligned} ln(Q(T_2)) &= -\frac{\Delta G^\circ(T_2)}{RT_2}, \\ ln(Q(T_1)) &= -\frac{\Delta G^\circ(T_1)}{RT_1}, \end{aligned}$$

we obtain, substituting into (22), canceling R, and performing the integration, if ΔH° is temperature independent, that;

$$\frac{\Delta G^\circ(T_2)}{T_2} - \frac{\Delta G^\circ(T_1)}{T_1} = -\int_{T_1}^{T_2} \frac{\Delta H^\circ}{T^2} = \Delta H^\circ(\frac{1}{T_2} - \frac{1}{T_1}). \tag{23}$$

For the fifth claim, rearrange (23). If D_c intersects the line $P = P^\circ$ at (T_1, P°), for the sixth (16) and seventh claims, we have, using Lemma 3 and the fact from Lemma 5 that $Q(T_1, P^\circ) = 1$;

$$\begin{aligned} (\frac{\partial G}{\partial \xi})_{T_2,P} &= \Delta G^\circ(T_2) + RT_2 ln(Q(T_2, P)) \\ &= (\frac{\partial G}{\partial \xi})_{T_1,P^\circ} \\ &= \Delta G^\circ(T_1) + RT_1 ln(Q(T_1, P^\circ)) \\ &= \Delta G^\circ(T_1) = c, \end{aligned}$$

so that, again rearranging, we obtain the result. Along D_c, we have, using Lemma 3, that;

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

so that, using the first part;

$$\begin{aligned}\frac{dln(Q)}{dT} &= \frac{d}{dT}(\frac{c-\Delta G^\circ}{RT})\\ &= \frac{-c}{RT^2}+\frac{d}{dT}(\frac{-\Delta G^\circ}{RT})\\ &= \frac{\Delta H^\circ - c}{RT^2},\end{aligned}$$

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 3;

$$\begin{aligned}&ln(Q(T_2)) = \frac{c-\Delta G^\circ(T_2)}{RT_2},\\ &ln(Q(T_1)) = 0,\end{aligned}$$

so that;

$$\begin{aligned}ln(Q(T_2)) &= ln(Q(T_2)) - ln(Q(T_1))\\ &= \frac{c-\Delta G^\circ(T_2)}{RT_2}\\ &= \frac{\Delta G^\circ(T_1)-\Delta G^\circ(T_2)}{RT_2}\\ &= \frac{1}{R}\int_{T_1}^{T_2}\frac{\Delta H^\circ - c}{T^2}dT\\ &= \frac{-1}{R}(\Delta H^\circ - c)(\frac{1}{T_2}-\frac{1}{T_1}),\end{aligned}$$

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 7. *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

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

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

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

and the dynamic equilibrium paths are given by;

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

for $c \in \mathcal{R}_{\geq 0}$*, see Definition 1, while the quasi-chemical equilibrium paths are given by;*

$$\lambda + \epsilon ln(P') + \beta T_2 = c,$$

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 6, 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 5 and the proof of Lemma 6, we have that

$$\begin{aligned}(\frac{\partial(\frac{dG}{d\xi})_{T,P}}{\partial T})_P &= (\frac{\partial(\sum_{i=1}^{c}\nu_i\mu_i)}{\partial T})_P \\ &= \sum_{i=1}^{c}\nu_i(\frac{\partial\mu_i}{\partial T})_P \\ &= \sum_{i=1}^{c}\nu_i(\frac{\partial\mu_i}{\partial T})_{P,n} \\ &= -\sum_{i=1}^{c}\nu_i\overline{S}_{m,i}. \end{aligned} \tag{24}$$

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 can assume that the liquid mixture is in thermal equilibrium with a mixture of ideal gases in the vapour phase, and using the ideal gas law, the definition of temperature for ideal gases, obtain the calculation of internal energy for the mixture;

$$U(T,P,n_1,\ldots,n_c) = \sum_{i=1}^{c}(\frac{3}{2}N_A n_i kT - N_A n_i m_i \rho_i),$$

where m_i is the molecular mass of species i, ρ_i is the specific latent heat of evaporation of species i, which we assume is independent of temperature T. By a result in [11], using the fact that entropy difference is independent of path, see [9], we have that Q is independent of P. We then have;

$$\begin{aligned} dU &= \sum_{i=1}^{c}\frac{3}{2}N_A kT dn_i + \sum_{i=1}^{c}\frac{3}{2}N_A k n_i dT - \sum_{i=1}^{c}N_A m_i\rho_i dn_i, \\ dQ &= \sum_{i=1}^{c}\frac{3}{2}N_A kT dn_i + \sum_{i=1}^{c}\frac{3}{2}N_A k n_i dT - \sum_{i=1}^{c}N_A m_i\rho_i dn_i + dL, \\ \frac{dQ}{T} &= \sum_{i=1}^{c}\frac{3}{2}N_A k dn_i + \sum_{i=1}^{c}\frac{3}{2}N_A k n_i\frac{dT}{T} - \sum_{i=1}^{c}N_A m_i\rho_i\frac{dn_i}{T} + \frac{g(T,\overline{n})dT}{T} + \sum_{i=1}^{c}h_i(T,\overline{n})\frac{dn_i}{T}, \\ (\frac{dQ}{T})_{n',T,P} &= \frac{3}{2}N_A k dn_i - N_A m_i\rho_i\frac{dn_i}{T} + h_i(T,\overline{n})\frac{dn_i}{T}. \end{aligned}$$

It follows that

$$\overline{S}_{m,i} = \int_{\Delta n_i = 1} (\frac{dQ}{T})_{n',T,P} = \frac{3}{2} N_A k - \frac{N_A m_i \rho_i}{T} + \frac{k_i(T)}{T}. \tag{25}$$

So that, from (24);

$$\begin{aligned}
(\frac{\partial(\frac{dG}{d\xi})_{T,P}}{\partial T})_P &= -\sum_{i=1}^{c} \nu_i (\frac{3}{2} N_A k - \frac{N_A m_i \rho_i}{T}) - \sum_{i=1}^{c} \nu_i \frac{k_i(T)}{T} \\
&= -\frac{3}{2} N_A k (\sum_{i=1}^{c} \nu_i) + \frac{N_A}{T} \sum_{i=1}^{c} \nu_i \mu_i \rho_i - \sum_{i=1}^{c} \nu_i \frac{k_i(T)}{T} \\
&= -\frac{3}{2} N_A k (\sum_{i=1}^{c} \nu_i) + \frac{N_A}{T} \sum_{i=1}^{c} \nu_i \mu_i \rho_i - \frac{G(T)}{T}. \qquad (26)
\end{aligned}$$

From (26), which is uniform P, we see that $(\frac{dG}{d\xi})_{T,P}$ is of the form $\alpha(P) + \beta T + \gamma ln(T) - \int \frac{G(T)}{T}$, (B), where $\{\beta, \gamma\} \subset \mathcal{R}$, and, assuming that $(\frac{dG}{d\xi})_{T,P}$ is differentiable, $\alpha \in C^1(\mathcal{R})$. By a similar calculation, we have that

$$\begin{aligned}
(\frac{\partial(\frac{dG}{d\xi})_{T,P}}{\partial P})_T &= (\frac{\partial(\sum_{i=1}^{c} \nu_i \mu_i)}{\partial P})_T \\
&= \sum_{i=1}^{c} \nu_i (\frac{\partial \mu_i}{\partial P})_T \\
&= \sum_{i=1}^{c} \nu_i (\frac{\partial \mu_i}{\partial P})_{T,n} \\
&= \sum_{i=1}^{c} \nu_i (\frac{\partial V}{\partial n_i})_{T,P,n'} \\
&= \sum_{i=1}^{c} \nu_i \overline{V}_i \\
&= \sum_{i=1}^{c} \nu_i \frac{N_A m_i}{\kappa_i(T,P)}, \qquad (27)
\end{aligned}$$

where κ_i is the density of substance i. We also have that

$$P(\sum_{i=1}^{c} \nu_i \frac{N_A m_i}{\kappa_i(T,P)}) = P(\sum_{i=1}^{c} \nu_i \overline{V}_i) = G(T), \qquad (dL = PdV), \tag{28}$$

and from (27) and (28);

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

so that $G(T) = \epsilon$, $\alpha(P) = \lambda + \epsilon ln(P)$, $(\frac{dG}{d\xi})_{T,P}$ is of the form

$$\begin{aligned}
\alpha(P) + \beta T + \gamma ln(T) - \int \frac{G(T)}{T} &= \lambda + \epsilon ln(P) + \beta T + \gamma ln(T) - \epsilon ln(T) \\
&= \lambda + \epsilon ln(P) + \beta T + \sigma ln(T), \qquad (29)
\end{aligned}$$

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

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 11 and 12, 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 (29), 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 $\epsilon \neq 0$, for any $c \in \mathcal{R}$, we can solve the equation;

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

for any given $T > 0$ and an appropriate choice of $P(T)$. In particularly, there exists a component D_c projecting 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

$$\Delta G^\circ(T_2) = (\frac{\partial G}{\partial \xi})_{T,P}(T_2, P^\circ) = \lambda + \epsilon ln(P^\circ) + \beta T_2 + \sigma ln(T_2),$$

so that, equating coefficients;

$$\begin{aligned}
&\sigma = 0, \\
&\lambda + \epsilon ln(P^\circ) = \Delta H^\circ, \\
&\beta = \frac{(\Delta G^\circ(T_1) - \Delta H^\circ)}{T_1}, \\
&\Delta G^\circ(T_1) = \beta T_1 + \Delta H^\circ, \\
&\Delta G^\circ(T_2) = \beta T_2 + \Delta H^\circ.
\end{aligned}$$

We can then, using Lemma 3, obtain a formula for the activity coefficient;

$$Q(T_2, P') = e^{\frac{((\frac{\partial G}{\partial \xi})_{T,P}|_{T_2,P'} - \Delta G^\circ(T_2))}{RT_2}} e^{\frac{(\Delta H^\circ - \epsilon ln(P'^\circ) + \epsilon ln(P') + \beta T_2 - (\beta T_2 + \Delta H^\circ))}{RT_2}} = e^{\frac{\epsilon ln(\frac{P'}{P'^\circ})}{RT_2}}, \quad (30)$$

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 Definition 1 and Lemma 13, follows from a simple rearrangement of the formulas $Q(T_1, P') = c$, for some $c \in \mathcal{R}_{\geq 0}$, using (30), and $(\frac{dG}{d\xi})_{T,P} = c$, for some $c \in \mathcal{R}$, using (29), with $\sigma = 0$. □

Lemma 8. *With notation as in Lemma 7, 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 7, if T_0 is a solution to;

$$\lambda + \beta T + \sigma ln(T) = 0, \quad (31)$$

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 9. *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 (4) of Lemma 2, we have that

$$(\frac{\partial G}{\partial \xi})_{T,P} = (\frac{\partial G_{chem'}}{\partial \xi})_{T,P} + 2EF. \tag{32}$$

By Lemma 7, we have that $(\frac{\partial G_{chem'}}{\partial \xi})_{T,P}$ is independent of P, in particularly, we have that

$$(\frac{\partial G_{chem'}}{\partial \xi})_{T_1,P_1} = (\frac{\partial G_{chem'}}{\partial \xi})_{T_1,P_1^\circ}, \tag{33}$$

so that, combining (32) and (33), we obtain the result. □

Lemma 10. *For all $T_1 > 0, P_1 > 0$, we have*

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

Proof. Following the proof of Lemma 2, we have that

$$(\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1} = (\frac{\partial G_{chem'}}{\partial \xi})_{T,P}|_{T_1,P_1} + 2E(T_1, P_1)F, \tag{34}$$

$$\begin{aligned} 2E^\circ(T_1)F &= (\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1^\circ} - (\frac{\partial G_{chem'}}{\partial \xi})_{T,P}|_{T_1,P_1^\circ} \\ &= (\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1^\circ} - \Delta G^\circ_{chem'}(T_1). \end{aligned} \tag{35}$$

So from (34) and (35) and Lemma 3;

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

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

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

□

Definition 3 (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 $\gamma : [0,1] \rightarrow \mathcal{R}^{2+c}_{>0}$, such that if $n_i(t) = pr_{2+i}(t)$, for $1 \leq i \leq c$, then

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

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 §13. 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 $\gamma : [0,1] \rightarrow \mathcal{R}^{2+c}_{\geq 0}$ 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 11. *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 5, and the definition of activities for an ideal solution, we have that

$$1 = Q(T,P) = \prod_{i=1}^{c} a_i^{\nu_i} = \prod_{i=1}^{c} x_i^{\nu_i}, \tag{36}$$

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

$$n_i' = \frac{\nu_i n_c'}{\nu_c}, \quad n_i = \frac{\nu_i n_c}{\nu_c} + d_i, \tag{37}$$

we obtain that

$$\begin{aligned}
(\prod_{i=1}^{c} x_i^{\nu_i})' &= \sum_{i=1}^{c} \nu_i x_i^{\nu_i - 1} x_i' \prod_{j \neq i} x_j^{\nu_j} = \sum_{i=1}^{c} \nu_i x_i^{\nu_i - 1} x_i' x_i^{-\nu_i} = \sum_{i=1}^{c} \nu_i x_i^{-1} x_i' \\
&= \sum_{i=1}^{c} \nu_i \frac{n}{n_i} \frac{(n_i' n - n_i n')}{n^2} = \sum_{i=1}^{c} \nu_i (\frac{n_i'}{n_i} - \frac{n'}{n}) \\
&= \sum_{i=1}^{c-1} \frac{\nu_i^2 n_c'}{\nu_i n_c + \nu_c d_i} + \frac{\nu_c n_c'}{n_c} - \lambda (\frac{\sum_{i=1}^{c} n_i'}{\sum_{i=1}^{c} n_i}) \\
&= \sum_{i=1}^{c-1} \frac{\nu_i^2 n_c'}{\nu_i n_c + \nu_c d_i} + \frac{\nu_c n_c'}{n_c} - \lambda (\frac{(\sum_{i=1}^{c-1} \frac{\nu_i}{\nu_c} + 1) n_c'}{(\sum_{i=1}^{c-1} \frac{\nu_i}{\nu_c} + 1) n_c + \sum_{i=1}^{c-1} d_i}) = 0,
\end{aligned} \tag{38}$$

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

$$\begin{aligned}
\gamma_c &= \sum_{i=1}^{c-1} \nu_i^2 \alpha \prod_{j \neq i} \nu_j + \alpha \nu_c \prod_{i=1}^{c-1} \nu_i - \lambda \prod_{i=1}^{c-1} \nu_i \\
&= \alpha \delta \sum_{i=1}^{c-1} \nu_i + \alpha \delta \nu_c - \lambda \delta \\
&= \delta(\alpha(\sum_{i=1}^{c} \nu_i) - \lambda) \\
&= \delta \lambda (\alpha - 1).
\end{aligned}$$

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 (37), 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 (36), that

$$\prod_{i=1}^{c} n_i^{\nu_i} = n^{\sum_{i=1}^{c} \nu_i} = 1, \tag{39}$$

and, following the calculation (38), 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 $k \geq 0$, canceling 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 $k \geq 0$;

$$\sum_{i=1}^{c-1} \nu_i^{k+2} g_i^{k+1} + \nu_c = \sum_{i=1}^{c-1} \nu_i (\nu_i g_i)^{k+1} + \nu_c = 0. \tag{40}$$

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

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

implies

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

Then if $n_c' \neq 0$, we must have that $\nu_i = -1$, $d_i = 0$. Re-scaling each ν_i by a factor of 2, we still have the conditions (36), (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 $k \rightarrow \infty$, 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;

$$\sum_{1 \leq i \leq c} \nu_i = \sum_{i \in I_j} \nu_i + \nu_j = \nu_j, \quad \text{for} \quad 1 \leq j \leq c,$$

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 5 that $Q(T, P^\circ) = 1$. $\square$

Definition 4. 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 12. *For every smooth curve $W \subset \mathcal{R}^2$, there exists a locally feasible path $\gamma : [0,1] \rightarrow \mathcal{R}^{2+c}$ with $pr_{12}(\gamma) \subset W$.*

Proof. As W is smooth, we can choose a local parametrization $\delta : [0,1] \rightarrow W$. 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 §13. We have that

$$\prod_{i=1}^{c} x_i^{\nu_i}(t) = \epsilon(t), \tag{41}$$

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

$$\alpha n_c^{\kappa}+r(n_c)=\epsilon(t)(\beta n_c^{\kappa}+s(n_c)), \tag{42}$$

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 (42) by $n_c^{\kappa}>0$, we obtain

$$\alpha+r_1(\frac{1}{n_c})=\epsilon(t)(\beta+s_1(\frac{1}{n_c})), \tag{43}$$

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 $r_1=\sum_{j=0}^{\kappa}c_jx^j$, $deg(s_1)\leq\kappa+\nu_c<\kappa$, so that $lim_{x\rightarrow\infty}\frac{\alpha+r_1(x)}{\beta+s_1(x)}=\infty$.

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 $\frac{-\nu_c d_{i_0}}{\nu_{i_0}}\neq\frac{-\nu_c d_{i_0}}{w}$,(1). 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 $lim_{x\rightarrow\infty}\frac{\alpha+r_1(x)}{\beta+s_1(x)}=\infty$ 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

$$n_i(0)=\frac{\nu_i}{\nu_c}n_c(0)+d_i=\frac{\nu_i}{\nu_c}\frac{1}{v_0}+d_i>0,\quad\text{as well, for}\quad i+1\leq i\leq p-1, \tag{44}$$

By (43), 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 un-ramified at $(v_0,0)$, so that we can apply the inverse function theorem, see [10], to obtain a real branch $\gamma(y)$ with $\gamma(0)=v_0$ and

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

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

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

---

[1] 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 §13, 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;

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

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 $r(x)$.

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 (44), 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 (41), 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 13. *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 11. Now follow through Lemma 11, 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

$$(\prod_{i=1}^{c} x_i^{\nu_i})'|_0 = Q(\gamma(t))'|_0 = (grad(Q)|_{\gamma(0)} \centerdot \gamma'(0)) \neq 0,$$

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 4 and the proof of Lemma 11, 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 14. *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 $\gamma : [0, 1] \rightarrow (T, P, n_1, \ldots n_c)$ 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 5 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 5 that $Q = 1$ iff $(\frac{\partial G}{\partial \xi})|_{T,P} - \Delta G^\circ = 0$. The second claim is clear from Lemma 13.

For the third claim, we have, by Lemma 5, 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 13, $pr_{12}(\gamma) \subset C_c$, 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 11, so that $P = P^\circ$ lies in C_1. It follows, by Lemma 13, that a feasible path γ with $pr_{12}(\gamma) \subset P = P^\circ$ is a dynamic equilibrium path. □

3. Ideal solutions

Remark 1. We have, using the phase rule for an ideal solution in equilibrium with its vapour, and using the ideal gas law, see [8], that

$$\begin{aligned}\mu_i^{(g)} &= \mu_i^{\circ(g)} + RTln(\frac{P_i}{P^\circ}),\\ \mu_i^{(sol)} &= \mu_i^{\circ(sol)} + RTln(\frac{P_i}{P^\circ}).\end{aligned} \tag{45}$$

By the definition of an ideal solution, we have that

$$\mu_i = \mu_i^* + RTln(x_i), \tag{46}$$

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 [7], combined with (46), we obtain;

$$\mu_i = \mu_i^* + RTln(x_i) = \mu_i^* + RTln(\frac{P_i}{P_i^*}) = \mu_i^* + RTln(\frac{P_i}{P^\circ}) - RTln(\frac{P_i^*}{P^\circ}). \tag{47}$$

Combining (45) and (47), we obtain that

$$\begin{aligned}\mu_i^* &= \mu_i - RTln(\frac{P_i}{P^\circ}) + RTln(\frac{P_i^*}{P^\circ})\\ &= (\mu_i^\circ + RTln(\frac{P_i}{P^\circ})) - RTln(\frac{P_i}{P^\circ}) + RTln(\frac{P_i^*}{P^\circ})\\ &= \mu_i^\circ + RTln(\frac{P_i^*}{P^\circ}).\end{aligned} \tag{48}$$

Letting $P_i^* = P^\circ$, we obtain that $\mu_i^*(T,P') = \mu_i^\circ$, (48), where (T,P') is the temperature and pressure at which the equilibrium pressure $P_i'^* = P^\circ$. From (46), the fact that $\mu_i^*(T,P) \simeq \mu_i^*(T,P')$ and (48), we obtain that

$$\mu_i \simeq \mu_i^\circ + RTln(x_i), \tag{49}$$

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 $n_i(T,P) \rightarrow 0$ as $P \rightarrow P^\circ$, so that $x_i = \frac{n_i}{n} \rightarrow 1$, 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 [7], 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 [7], that

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

so that

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

where $\epsilon = \mu_i^*(T,P) - \mu_i^*(T,P_i^*)$, so that (47) becomes;

$$\mu_i = \mu_i^* + RTln(x_i) = \mu_i^* + RTln(\frac{P_i}{P^\circ}) - RTln(\frac{P_i^*}{P^\circ}) - \epsilon. \tag{50}$$

Combining (45) and (50), we obtain that

$$\begin{aligned}\mu_i^* &= \mu_i - RTln(\frac{P_i}{P^\circ}) + RTln(\frac{P_i^*}{P^\circ}) + \epsilon \\ &= (\mu_i^\circ + RTln(\frac{P_i}{P^\circ})) - RTln(\frac{P_i}{P^\circ}) + RTln(\frac{P_i^*}{P^\circ}) + \epsilon \\ &= \mu_i^\circ + RTln(\frac{P_i^*}{P^\circ}) + \epsilon. \end{aligned} \tag{51}$$

Letting $P_i^* = P^\circ$ again, we obtain that

$$\mu_i^*(T,P') = \mu_i^\circ + \epsilon. \tag{52}$$

From (46) and (52), 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 1, 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;

$$\begin{aligned}\mu_i^*(T,P) - \mu_i^*(T,P_i^*) &= \frac{G(T,P,n) - G(T,P_i^*,n)}{n} = \frac{1}{n}\int_{P_i^*}^P dG = \frac{1}{n}\int_{P_i^*}^P VdP \\ &= \frac{1}{n}\int_{P_i^*}^P \frac{nN_A m_i}{\kappa_i(T,P)} dP \simeq \frac{N_A m_i(P-P_i^*)}{\kappa} = V_{m,i}(P-P_i^*),\end{aligned}$$

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

$$\gamma_i(P) \simeq V_{m,i}(2P - P_i^* - P') \simeq 0.$$

Now, we reformulate Lemmas 3, 5, 6 and 7 with this error term.

Lemma 15. *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 $\epsilon(P) = \sum_{i=1}^c \nu_i\gamma_i(P) \simeq 0$ *and* $\gamma_i(P) \simeq 0$ *is the error term for the i'th uncharged species in Remark 1.*

Proof. By Lemma 5, we have that

$$(\frac{\partial G}{\partial \xi})_{T,P} = \sum_{i=1}^c \nu_i\mu_i, \qquad \Delta G^\circ = \sum_{i=1}^c \nu_i\mu_i^\circ. \tag{53}$$

Using (53), the fact that $\mu_i = \mu_i^\circ + RTln(a_i) + \gamma_i$, and Definition 1, we have that

$$\begin{aligned}(\frac{\partial G}{\partial \xi})_{T,P} - \Delta G^\circ &= \sum_{i=1}^c \nu_i(\mu_i - \mu_i^\circ) = \sum_{i=1}^c \nu_i(\mu_i^\circ + RTln(a_i) + \gamma_i - \mu_i^\circ) \\ &= \sum_{i=1}^c \nu_i RTln(a_i) + \sum_{i=1}^c \nu_i\gamma_i = RTln(\prod_{i=1}^c a_i^{\nu_i}) + \sum_{i=1}^c \nu_i\gamma_i = RTln(Q) + \epsilon.\end{aligned}$$

□

Lemma 16. *For an ideal solution, we have, using the definition of* $\epsilon(P)$ *in Lemma 3, and the error terms* $\gamma_i(P), 1 \leq i \leq c$ *in Remark 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), *then* $Q(T,P) = e^{\frac{-\epsilon(P)}{RT}} \simeq 1$ *and* $E = E^\circ$. *Conversely, if* $Q(T,P) = e^{\frac{-\epsilon(P)}{RT}} \simeq 1$ *and chemical equilibrium exists at* (T,P°) *then chemical equilibrium exists at* (T,P).

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

We always have that $Q(T,P^\circ) = e^{\frac{-\delta}{RT}} \simeq 1$, *where* $\delta = \epsilon(P^\circ) = \sum_{i=1}^{c} \nu_i \gamma_i(P^\circ)$.

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

$$dn_i = \nu_i d\xi, \qquad (1 \leq i \leq c). \tag{54}$$

By Lemma 1, fixing T and P, and using (54), we have that

$$dG = \sum_{i=1}^{c} \mu_i dn_i = (\sum_{i=1}^{c} \mu_i \nu_i) d\xi, \tag{55}$$

so that

$$(\frac{\partial G}{\partial \xi})_{T,P} = \sum_{i=1}^{c} \mu_i \nu_i. \tag{56}$$

The second claim follows 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 (55) and (56), we have that

$$dG = (\frac{\partial G}{\partial \xi})_{T,P} = 0, \qquad \text{(independently of } \xi\text{)}. \tag{57}$$

At chemical equilibrium (T,P°), using the first and second claims, and (57), 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, that $RTln(Q) = -\epsilon \simeq 0$, so that $Q(T,P) = e^{\frac{-\epsilon(P)}{RT}} \simeq 1$, and, by Lemma 20, that $E - E^\circ = -\frac{RTln(Q)}{2F} - \frac{\epsilon(P)}{2F} = \frac{\epsilon(P)}{2F} - \frac{\epsilon(P)}{2F} = 0$. For the converse, we have by Lemma 3, using the fact that $Q(T,P) = e^{\frac{-\epsilon(P)}{RT}} \simeq 1$;

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

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

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

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

For the penultimate claim, in one direction, use Lemma 3, 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

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

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

Lemma 17. *Along a chemical equilibrium path, we have that*

$$\begin{aligned} ln(\frac{Q(T_2)}{Q(T_1)}) &= \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^\circ}{T^2} dT + + \frac{1}{R}(\frac{\epsilon(P(T_1))}{T_1} - \frac{\epsilon(P(T_2))}{T_2}), \\ \frac{\Delta G^\circ(T_2)}{T_2} - \frac{\Delta G^\circ(T_1)}{T_1} &= -\int_{T_1}^{T_2} \frac{\Delta H^\circ}{T^2} dT. \end{aligned}$$

In particularly, if ΔH° is temperature independent

$$\begin{aligned} ln(\frac{Q(T_2)}{Q(T_1)}) &= -\frac{\Delta H^\circ}{R}(\frac{1}{T_2} - \frac{1}{T_1}) + \frac{1}{R}(\frac{\epsilon(P(T_1))}{T_1} - \frac{\epsilon(P(T_2))}{T_2}), \\ \frac{\Delta G^\circ(T_2)}{T_2} - \frac{\Delta G^\circ(T_1)}{T_1} &= \Delta H^\circ(\frac{1}{T_2} - \frac{1}{T_1}), \\ \Delta G^\circ(T_1) &= \frac{T_1}{T_2}\Delta G^\circ(T_2) - (\frac{T_1}{T_2} - 1)\Delta H^\circ. \end{aligned}$$

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

$$\begin{aligned} Q(T_2, P) &= e^{\frac{\Delta G^\circ(T_1) - \Delta G^\circ(T_2) - \epsilon(P(T_2))}{RT_2}}, \qquad (58) \\ c &= \Delta G^\circ(T_1), \\ ln(\frac{Q(T_2)}{Q(T_1)}) &= ln(Q(T_2)) = \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^\circ - c}{T^2} dT - (\frac{\epsilon(P(T_2))}{RT_2} - \frac{\epsilon(P(T_1))}{RT_1}), \\ \frac{\Delta G^\circ(T_2) - \Delta G^\circ(T_1)}{T_2} &= -\int_{T_1}^{T_2} \frac{\Delta H^\circ - c}{T^2} dT, \end{aligned}$$

and if ΔH° is temperature independent;

$$ln(\frac{Q(T_2)}{Q(T_1)}) = ln(Q(T_2)) = -(\frac{\Delta H^\circ - c}{R})(\frac{1}{T_2} - \frac{1}{T_1}) - (\frac{\epsilon(P(T_2))}{RT_2} - \frac{\epsilon(P(T_1))}{RT_1}), \qquad (59)$$

$$\frac{\Delta G^\circ(T_2) - \Delta G^\circ(T_1)}{T_2} = (\Delta H^\circ - c)(\frac{1}{T_2} - \frac{1}{T_1}), \qquad (60)$$

$$\Delta G^\circ(T_1) = \frac{T_1}{T_2}\Delta G^\circ(T_2) - \Delta H^\circ(\frac{T_1}{T_2} - 1). \qquad (61)$$

Proof. By Lemma 5, 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;

$$\frac{d(\Delta G^\circ)}{dT} = -\sum_{i=1}^{c} \nu_i \overline{S}_i^\circ == -\sum_{i=1}^{c} \nu_i \overline{S}_{m,i}^\circ = -\Delta S^\circ. \tag{62}$$

Using the product rule, (62) and the definition of enthalpy, we have that

$$\frac{d}{dT}(\frac{\Delta G^\circ}{T}) = \frac{1}{T}\frac{d(\Delta G^\circ)}{dT} - \frac{1}{T^2}\Delta G^\circ = -\frac{\Delta S^\circ}{T} - \frac{\Delta G^\circ}{T^2} = -\frac{\Delta(ST+G)^\circ}{T^2} = -\frac{\Delta H^\circ}{T^2}. \tag{63}$$

By Lemma 16, along a chemical equilibrium path, we have that $Q = e^{\frac{-\Delta G^\circ - \epsilon(P)}{RT}}$, so that $ln(Q) = \frac{-\Delta G^\circ - \epsilon(P)}{RT}$. It follows from (63) 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

$$\begin{aligned} ln(\frac{Q(T_2)}{Q(T_1)}) &= ln(Q)(T_2) - ln(Q)(T_1) \\ &= \int_{T_1}^{T_2} \frac{dln(Q)}{dT} dT \\ &= \frac{1}{R}\int_{T_1}^{T_2} [\frac{\Delta H^\circ}{T^2} - \frac{d}{dT}(\frac{\epsilon(P)}{RT})]dT \\ &= \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta H^\circ}{RT_1} - (\frac{\epsilon(P(T_2))}{RT_2} - \frac{\epsilon(P(T_1))}{RT_1}), \end{aligned} \tag{64}$$

so that, rearranging, we obtain the first claim. Using the fact, by Lemma 15, that

$$\begin{aligned} ln(Q(T_2)) &= \frac{-\Delta G^\circ(T_2) - \epsilon(P(T_2))}{RT_2}, \\ ln(Q(T_1)) &= \frac{-\Delta G^\circ(T_1) - \epsilon(P(T_1))}{RT_1}, \end{aligned}$$

we obtain, substituting into (64), canceling R, and performing the integration, if ΔH° is temperature independent, that

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

so that

$$\frac{\Delta G^\circ(T_2)}{T_2} - \frac{\Delta G^\circ(T_1)}{T_1} = \Delta H^\circ(\frac{1}{T_2} - \frac{1}{T_1}). \tag{65}$$

For the fifth claim, rearrange (65). If D_c intersects the line $P = P^\circ$ at (T_1, P°), for the sixth (58) and seventh claims, we have, using Lemma 3 and the fact from Lemma 16 that $Q(T_1, P^\circ) = e^{\frac{-\delta}{RT_1}}$;

$$\begin{aligned} (\frac{\partial G}{\partial \xi})_{T_2,P} &= \Delta G^\circ(T_2) + RT_2 ln(Q(T_2,P)) + \epsilon(P(T_2)) = (\frac{\partial G}{\partial \xi})_{T_1,P^\circ} \\ &= \Delta G^\circ(T_1) + RT_1 ln(Q(T_1,P^\circ)) + \epsilon(P(T_1)) \\ &= \Delta G^\circ(T_1) + RT_1 ln(Q(T_1,P^\circ)) + \epsilon(P^\circ) \\ &= \Delta G^\circ(T_1) - \delta + \epsilon(P^\circ) \\ &= \Delta G^\circ(T_1) = c, \end{aligned}$$

so that, again rearranging, we obtain the result. Along D_c, we have, using Lemma 3, that

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

so that, using the first part;

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

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

$$\begin{aligned} ln(Q(T_2)) - ln(Q(T_1)) &= ln(Q(T_2)) + \frac{\delta}{RT_1} \\ &= \frac{1}{R}\int_{T_1}^{T_2} [\frac{\Delta H^\circ - c}{T^2} - \frac{d}{dT}(\frac{\epsilon(P(T))}{RT})]dT \\ &= \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^\circ - c}{T^2} dT - (\frac{\epsilon(P(T_2))}{RT_2} - \frac{\epsilon(P(T_1))}{RT_1}). \end{aligned}$$

We have that, by Lemma 15;

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

so that

$$\begin{aligned} ln(Q(T_2)) - ln(Q(T_1)) &= \frac{c - \Delta G^\circ(T_2) - \epsilon(P(T_2))}{RT_2} + \frac{\delta}{RT_1} \\ &= \frac{\Delta G^\circ(T_1) - \Delta G^\circ(T_2) - \epsilon(P(T_2))}{RT_2} + \frac{\delta}{RT_1} \\ &= \frac{1}{R}\int_{T_1}^{T_2} [\frac{\Delta H^\circ - c}{T^2} - (\frac{\epsilon(P(T_2))}{RT_2} - \frac{\epsilon(P(T_1))}{RT_1}) \\ &= \frac{-1}{R}(\Delta H^\circ - c)(\frac{1}{T_2} - \frac{1}{T_1}) - (\frac{\epsilon(P(T_2))}{RT_2} - \frac{\delta}{RT_1}), \end{aligned}$$

so that, canceling 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 18. *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;*

$$\Delta G^\circ(T_2) = T_2(\frac{(\Delta G^\circ(T_1) - \Delta H^\circ)}{T_1}) + \Delta H^\circ, \quad for \quad T_2 \in I.$$

If $\epsilon \neq 0$, have that; $(\frac{dG}{d\xi})_{T,P} = \lambda + \epsilon ln(P) + \beta T$ where $\{\lambda, \epsilon, \beta\} \subset \mathcal{R}$ and $\{\beta, \epsilon\}$ can be effectively determined, and we have that the activity coefficient is given by; $Q(T_1, P') = e^{\frac{\epsilon ln(\frac{P'}{P'^\circ}) - \epsilon(P')}{RT_1}}$ and the dynamic equilibrium paths are *given by;* $(\frac{P'}{P'^{\circ}})^{\frac{\epsilon}{RT_1}} = ce^{\epsilon(P')}$ *for* $c \in \mathcal{R}_{\geq 0}$*, see Definition 1, while the quasi-chemical equilibrium paths are given by;* $\lambda + \epsilon ln(P') + \beta T_1 = c$ *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;* $Q(T_1, P') = e^{\frac{-\epsilon(P')}{RT_1}}$.

The dynamic equilibrium paths are given by; $e^{\frac{-\epsilon(P')}{RT_1}} = c$ *for* $c \in \mathcal{R}_{\geq 0}$*, see Definition 1, while the quasi-chemical equilibrium paths are given by;* $\lambda + \epsilon ln(P') + \beta T_1 = c$ *for* $c \in \mathcal{R}$.

Proof. For the first claim, by Lemma 17, 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 16 and the proof of Lemma 7, we have that

$$(\frac{\partial(\frac{dG}{d\xi})_{T,P}}{\partial T})_P = (\frac{\partial(\sum \nu_i \mu_i)}{\partial T})_P = \sum \nu_i(\frac{\partial \mu_i}{\partial T})_P = \sum \nu_i(\frac{\partial \mu_i}{\partial T})_{P,n} = -\sum \nu_i \overline{S}_{m,i}. \tag{66}$$

Again, 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. We can assume that the liquid mixture is in thermal equilibrium with a mixture of ideal gases in the vapour phase, and using the ideal gas law, the definition of temperature for ideal gases, obtain the calculation of internal energy for the mixture;

$$U(T, P, n_1, \ldots, n_c) = \sum_{i=1}^{c}(\frac{3}{2}N_A n_i kT - N_A n_i m_i \rho_i),$$

where m_i is the molecular mass of species i, ρ_i is the specific latent heat of evaporation of species i, which we assume is independent of temperature T. By a result in [11], using the fact that entropy difference is independent of path, we have that Q is independent of P. We then have

$$\begin{aligned}
dU &= \sum_{i=1}^{c}\frac{3}{2}N_A kT dn_i + \sum_{i=1}^{c}\frac{3}{2}N_A k n_i dT - \sum_{i=1}^{c} N_A m_i \rho_i dn_i,\\
dQ &= \sum_{i=1}^{c}\frac{3}{2}N_A kT dn_i + \sum_{i=1}^{c}\frac{3}{2}N_A k n_i dT - \sum_{i=1}^{c} N_A m_i \rho_i dn_i + dL,\\
\frac{dQ}{T} &= \sum_{i=1}^{c}\frac{3}{2}N_A k dn_i + \sum_{i=1}^{c}\frac{3}{2}N_A k n_i \frac{dT}{T} - \sum_{i=1}^{c} N_A m_i \rho_i \frac{dn_i}{T} + \frac{g(T,\overline{n})dT}{T} + \sum_{i=1}^{c} h_i(T,\overline{n})\frac{dn_i}{T},\\
(\frac{dQ}{T})_{n',T,P} &= \frac{3}{2}N_A k dn_i - N_A m_i \rho_i \frac{dn_i}{T} + h_i(T,\overline{n})\frac{dn_i}{T}.
\end{aligned}$$

It follows that

$$\overline{S}_{m,i} = \int_{\Delta n_i = 1}(\frac{dQ}{T})_{n',T,P} = \frac{3}{2}N_A k - \frac{N_A m_i \rho_i}{T} + \frac{k_i(T)}{T}. \tag{67}$$

So that, from (66)

$$\begin{aligned}
(\frac{\partial(\frac{dG}{d\xi})_{T,P}}{\partial T})_P &= -\sum_{i=1}^{c}\nu_i(\frac{3}{2}N_A k - \frac{N_A m_i \rho_i}{T}) - \sum_{i=1}^{c}\nu_i \frac{k_i(T)}{T}\\
&= -\frac{3}{2}N_A k(\sum_{i=1}^{c}\nu_i) + \frac{N_A}{T}\sum_{i=1}^{c}\nu_i \mu_i \rho_i - \sum_{i=1}^{c}\nu_i \frac{k_i(T)}{T}\\
&= -\frac{3}{2}N_A k(\sum_{i=1}^{c}\nu_i) + \frac{N_A}{T}\sum_{i=1}^{c}\nu_i \mu_i \rho_i - \frac{G(T)}{T}.
\end{aligned} \tag{68}$$

From (68), which is uniform P, we see that $(\frac{dG}{d\xi})_{T,P}$ is of the form

$$\alpha(P) + \beta T + \gamma ln(T) - \int \frac{G(T)}{T}, \tag{69}$$

where $\{\beta, \gamma\} \subset \mathcal{R}$, and, assuming that $(\frac{dG}{d\xi})_{T,P}$ is differentiable, $\alpha \in C^1(\mathcal{R})$. By a similar calculation, we have that

$$(\frac{\partial(\frac{dG}{d\xi})_{T,P}}{\partial P})_T = (\frac{\partial(\sum \nu_i \mu_i)}{\partial P})_T = \sum_{i=1}^{c} \nu_i (\frac{\partial \mu_i}{\partial P})_T = \sum_{i=1}^{c} \nu_i (\frac{\partial \mu_i}{\partial P})_{T,n} = \sum_{i=1}^{c} \nu_i (\frac{\partial V}{\partial n_i})_{T,P,n'} = \sum_{i=1}^{c} \nu_i \overline{V}_i = \sum_{i=1}^{c} \nu_i \frac{N_A m_i}{\kappa_i(T,P)}, \tag{70}$$

where κ_i is the density of substance i. We also have that

$$P(\sum_{i=1}^{c} \nu_i \frac{N_A m_i}{\kappa_i(T,P)}) = P(\sum_{i=1}^{c} \nu_i \overline{V}_i) = G(T), \qquad (dL = PdV), \tag{71}$$

and from (70),(69) and (71), we have that

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

so that $G(T) = \epsilon$, $\alpha(P) = \lambda + \epsilon ln(P)$, $(\frac{dG}{d\xi})_{T,P}$ is of the form;

$$\alpha(P) + \beta T + \gamma ln(T) - \int \frac{G(T)}{T} = \lambda + \epsilon ln(P) + \beta T + \gamma ln(T) - \epsilon ln(T) = \lambda + \epsilon ln(P) + \beta T + \sigma ln(T), \tag{72}$$

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

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 $RT_1 ln(Q(T_1, P) = -\epsilon(P)$, so that

$$Q(T_1, P) = e^{\frac{-\epsilon(P)}{RT_1}}. \tag{73}$$

From (72), we have that

$$(\frac{dG}{d\xi})_{T,P} = \lambda + \beta T + \sigma ln(T). \tag{74}$$

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 (73) and (74).

If $\epsilon \neq 0$, for any $c \in \mathcal{R}$, we can solve the equation;

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

for any given $T > 0$ and an appropriate choice of $P(T)$. In particularly, there exists a component D_c projecting 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;

$$\lambda + \epsilon ln(P^\circ) + \beta T + \sigma ln(T) = c, \tag{75}$$

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

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

we can again solve the Eq. (75) 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 (72), that

$$\Delta G^\circ(T_2) = (\frac{\partial G}{\partial \xi})_{T,P}(T_2, P^\circ) = \lambda + \epsilon ln(P^\circ) + \beta T_2 + \sigma ln(T_2),$$

so that, equating coefficients;

$$\begin{aligned}
\sigma &= 0,\\
\lambda + \epsilon ln(P^\circ) &= \Delta H^\circ,\\
\beta &= \frac{(\Delta G^\circ(T_1) - \Delta H^\circ)}{T_1},\\
\Delta G^\circ(T_1) &= \beta T_1 + \Delta H^\circ.
\end{aligned}$$

We can then, using Lemma 15, obtain a formula for the activity coefficient;

$$Q(T_1, P') = e^{\frac{((\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P'} - \Delta G^\circ(T_1)) - \epsilon(P')}{RT_1}} = e^{\frac{(\Delta H^\circ - \epsilon ln(P'^\circ) + \epsilon ln(P') + \beta T_1 - (\beta T_1 + \Delta H^\circ)) - \epsilon(P')}{RT_1}} = e^{\frac{\epsilon ln(\frac{P'}{P'^\circ}) - \epsilon(P')}{RT_1}}, \tag{76}$$

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 1 and Lemma 13, follows from a simple rearrangement of the formulas $Q(T_1, P') = c$, for some $c \in \mathcal{R}_{\geq 0}$, using (76), and $(\frac{dG}{d\xi})_{T,P} = c$, for some $c \in \mathcal{R}$, using (72), with $\sigma = 0$. □

Lemma 19. *Let notation be as in Lemma 7, then if* $\epsilon \neq 0$, *with* $Q(T,P) = (\frac{P}{P^\circ})^{\frac{\epsilon}{RT}} e^{\frac{-\epsilon(P)}{RT}}$, *then, using the definition of grad in [2];*

$$grad(Q)(T,P) = (\frac{-\epsilon ln(\frac{P}{P^\circ}) + \epsilon(P)}{RT^2}(\frac{P}{P^\circ})^{\frac{\epsilon}{RT}} e^{\frac{-\epsilon(P)}{RT}}, \frac{\frac{\epsilon}{P} - \epsilon'(P)}{RT}(\frac{P}{P^\circ})^{\frac{\epsilon}{RT}} e^{\frac{-\epsilon(P)}{RT}}).$$

In particular the paths of maximal reaction, for the region $|grad(Q)(T,P)| > 1$, $Q(T,P) > 0$, *are given by* $\int \frac{\epsilon P ln(\frac{P}{P^\circ}) - P\epsilon(P)}{P\epsilon'(P) - \epsilon} dP = -\frac{T^2}{2} + c$ *for* $c \in \mathcal{R}$.

If $\epsilon(P) = 0$; *then* $grad(Q)(T,P) = (\frac{-\epsilon ln(\frac{P}{P^\circ})}{RT^2}(\frac{P}{P^\circ})^{\frac{\epsilon}{RT}}, \frac{\epsilon}{RTP}(\frac{P}{P^\circ})^{\frac{\epsilon}{RT}})$ *and the paths of maximal reaction, for the region* $|grad(Q)(T,P)| > 1$, $Q(T,P) > 0$, *are given by* $P^2(\frac{ln(P)}{2} - \frac{ln(P^\circ)}{2} - \frac{1}{4}) + \frac{T^2}{2} = c$ *for* $c \in \mathcal{R}$.

If $\epsilon = 0$, *with* $Q(T,P) = e^{\frac{-\epsilon(P)}{RT}}$, *then* $grad(Q)(T,P) = (\frac{\epsilon(P)}{RT^2} e^{\frac{-\epsilon(P)}{RT}}, -\frac{\epsilon'(P)}{RT} e^{\frac{-\epsilon(P)}{RT}})$ *and the paths of maximal reaction, for the region* $|grad(Q)(T,P)| > 1$, $Q(T,P) > 0$, *are given by* $\int \frac{\epsilon(P)}{\epsilon'(P)} dP = \frac{-T^2}{2} + c$ *for* $c \in \mathcal{R}$.

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 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;

$$\prod_{i=1}^{c} x_i^{\nu_i}(t) = Q(\gamma_{12}(t)) = \prod_{i=1}^{c} (\frac{\nu_i \xi(t) + n_{i,0}}{\alpha \xi(t) + \beta})^{\nu_i} = \frac{\prod_{i=1}^{c} (\nu_i \xi(t) + n_{i,0})^{\nu_i}}{(\alpha \xi(t) + \beta)^c} = G_\gamma(\xi(t)),$$

where $G_\gamma(x) = \frac{\prod_{i=1}^{c} (\nu_i x + n_{i,0})^{\nu_i}}{(\alpha x + \beta)^c}$. We have that $\xi(0) = 0$, and, as we can assume that $\beta > 0$, we have that

$$\begin{aligned}
G'_\gamma(0) &= \frac{\sum_{i=1}^{c} \nu_i (\prod_{j \neq i} n_{j,0})}{\beta^c} - \frac{c \prod_{j=1}^{c} n_{j,0}}{\beta^{c+1}} \\
&= \frac{1}{\beta^{c+1}} (\beta (\sum_{i=1}^{c} \nu_i (\prod_{j \neq i} n_{j,0}) - c \prod_{j=1}^{c} n_{j,0})) \\
&= \frac{\prod_{j=1}^{c} n_{j,0}}{\beta^{c+1}} (\beta \frac{\sum_{i=1}^{c} \nu_i}{n_{i,0}} - c) \\
&= \frac{\prod_{j=1}^{c} n_{j,0}}{\beta^{c+1}} (n_{init} \frac{\sum_{i=1}^{c} \nu_i}{n_{i,0}} - c) \\
&= \frac{\prod_{j=1}^{c} n_{j,0}}{\beta^{c+1}} (\sum_{i=1}^{c} \frac{\nu_i}{x_{i,init}} - c) \\
&= \frac{\prod_{j=1}^{c} n_{j,0}}{\beta^{c+1}} ((\sum_{i=1}^{c} \nu_i log(x_i))'_{init} - c) \\
&= \frac{\prod_{j=1}^{c} n_{j,0}}{\beta^{c+1}} (log(\prod_{i=1}^{c} x_i^{\nu_i})'_{init} - c) \\
&= \frac{\prod_{j=1}^{c} n_{j,0}}{\beta^{c+1}} (log(Q(\gamma_{12}(t)))'|_0 - c) \\
&= \frac{\prod_{j=1}^{c} n_{j,0}}{\beta^{c+1}} (\frac{grad(Q) \cdot \gamma'_{12}(0)}{Q(\gamma_{12}(0))} - c),
\end{aligned}$$

so that;

$$G'_\gamma(0) = 0, \quad \text{iff} \quad \frac{grad(Q) \cdot \gamma'_{12}(0)}{Q(\gamma_{12}(0))} = c,$$

which we can exclude by an appropriate parametrization of the feasible path γ, without altering the direction of $\gamma'_{12}(0)$. 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

$$\begin{aligned}
\xi'(0) &= (G_\gamma^{-1})'|_{Q(T_0,P_0)} grad(Q)(T_0,P_0) \cdot \gamma'_{12}(0) \\
&= \frac{grad(Q)(T_0,P_0) \cdot \gamma'_{12}(0)}{G'_\gamma(0)} \\
&= grad(Q)(T_0,P_0) \cdot \gamma'_{12}(0) \frac{\beta^{c+1}}{\prod_{j=1}^{c} n_{j,0}} \frac{Q(\gamma_{12}(0))}{grad(Q) \cdot \gamma'_{12}(0) - cQ(\gamma_{12}(0))} \\
&= \frac{\alpha_1 \beta_1 [grad(Q)(T_0,P_0) \cdot \gamma'_{12}(0)]}{grad(Q)(T_0,P_0) \cdot \gamma'_{12}(0) - c\beta_1},
\end{aligned}$$

where $\gamma_{12}(0) = (T_0, P_0)$, $\alpha_1(T_0, P_0) = \frac{\beta^{c+1}}{\prod_{j=1}^{c} n_{j,0}}$, $\beta_1(T_0, P_0) = Q(\gamma_{12}(0))$.

Writing $\gamma_{12}'(0) = \lambda(cos(\theta), sin(\theta))$, we have that

$$\xi'(0) = \frac{\lambda\alpha_1\beta_1[\frac{\partial Q}{\partial T}|_{(T_0,P_0)}cos(\theta) + \frac{\partial Q}{\partial P}|_{(T_0,P_0)}sin(\theta)]}{\lambda[\frac{\partial Q}{\partial T}|_{(T_0,P_0)}cos(\theta) + \frac{\partial Q}{\partial P}|_{(T_0,P_0)}sin(\theta)] - c\beta_1} = h(\lambda,\theta) = \frac{\lambda\alpha_1\beta_1 r(\theta)}{\lambda r(\theta) - c\beta_1},$$

where $r(\theta) = \frac{\partial Q}{\partial T}|_{(T_0,P_0)}cos(\theta) + \frac{\partial Q}{\partial P}|_{(T_0,P_0)}sin(\theta)$. We have that $\frac{\partial h}{\partial \lambda} = \frac{\alpha_1\beta_1 r(\theta)}{\lambda r(\theta) - c\beta_1} - \frac{\lambda\alpha_1\beta_1 r^2(\theta)}{(\lambda r(\theta) - c\beta_1)^2}$, so that $\frac{\partial h}{\partial \lambda} = 0$ iff $\alpha_1\beta_1 r(\theta)(\lambda r(\theta) - c\beta_1) - \lambda\alpha_1\beta_1 r^2(\theta) = 0$ iff $-c\alpha_1\beta_1^2 r(\theta) = 0$, so that, as $\alpha_1 \neq 0$, $Q(T_0, P_0) \neq 0$, and $(cos(\theta), sin(\theta))$ is not tangent to the dynamic equilibrium path at (T_0, P_0), then $h(\lambda, \theta)$ is monotonic in λ.

$$\frac{\partial h}{\partial \theta} = \frac{\lambda\alpha_1\beta_1 r'(\theta)}{\lambda r(\theta) - c\beta_1} - \frac{\lambda^2\alpha_1\beta_1 r'(\theta)}{(\lambda r(\theta) - c\beta_1)^2},$$

so that $\frac{\partial h}{\partial \theta} = 0$ iff $\lambda\alpha_1\beta_1 r'(\theta)(\lambda r(\theta) - c\beta_1) - \lambda^2\alpha_1\beta_1 r'(\theta) = 0$ iff $\lambda\alpha_1\beta_1(\lambda r(\theta) - c\beta_1) - \lambda^2\alpha_1\beta_1 = 0$ iff $r(\theta) = \frac{\lambda^2\alpha_1\beta_1 + c\lambda\alpha_1\beta_1^2}{\lambda^2\alpha_1\beta_1} = 1 + \frac{c\beta_1}{\lambda}$.

If $|1 + \frac{c\beta_1}{\lambda}| \leq |grad(Q)(T_0, P_0)|$, and $|grad(Q)(T_0, P_0)| > 1$, we can solve $r(\theta) = 1 + \frac{c\beta_1}{\lambda}$, for $\lambda > 0$, so that, when $r(\theta(\lambda)) = 1 + \frac{c\beta_1}{\lambda}$;

$$h(\lambda, \theta(\lambda)) = \frac{\lambda\alpha_1\beta_1(1 + \frac{c\beta_1}{\lambda})}{\lambda(1 + \frac{c\beta_1}{\lambda}) - c\beta_1} = \frac{\lambda\alpha_1\beta_1 + c\alpha_1\beta_1^2}{\lambda} = \alpha_1\beta_1 + \frac{c\alpha_1\beta_1^2}{\lambda} = \alpha_1\beta_1(1 + \frac{c\beta_1}{\lambda}),$$

so a maximum/minimum occurs when $|1 + \frac{c\beta_1}{\lambda}| = |grad(Q)(T_0, P_0)|$, in which case $(cos(\theta), sin(\theta))$ is parallel to $grad(Q)(T_0, P_0)$, and perpendicular to the tangent of the level curve of Q, through (T_0, P_0). We, therefore, have to solve the paired differential equation;

$$\frac{dT}{dt} = \frac{-\epsilon ln(\frac{P(t)}{P^\circ}) + \epsilon(P(t))}{RT(t)^2}(\frac{P(t)}{P^\circ})^{\frac{\epsilon}{RT(t)}} e^{\frac{-\epsilon(P(t))}{RT(t)}},$$
$$\frac{dP}{dt} = \frac{\frac{\epsilon}{P(t)} - \epsilon'(P(t))}{RT(t)}(\frac{P(t)}{P^\circ})^{\frac{\epsilon}{RT(t)}} e^{\frac{-\epsilon(P(t))}{RT(t)}},$$

so that

$$\frac{dP}{dT} = \frac{\frac{dP}{dt}}{\frac{dT}{dt}} = \frac{\frac{\frac{\epsilon}{P} - \epsilon'(P)}{RT}(\frac{P}{P^\circ})^{\frac{\epsilon}{RT}} e^{\frac{-\epsilon(P)}{RT}}}{\frac{-\epsilon ln(\frac{P}{P^\circ}) + \epsilon(P)}{RT^2}(\frac{P}{P^\circ})^{\frac{\epsilon}{RT}} e^{\frac{-\epsilon(P)}{RT}}} = \frac{T(\frac{\epsilon}{P} - \epsilon'(P))}{-\epsilon ln(\frac{P}{P^\circ}) + \epsilon(P)}.$$

Separating variables, we obtain that

$$\frac{\epsilon ln(\frac{P}{P^\circ}) - \epsilon(P)}{\epsilon'(P) - \frac{\epsilon}{P}} dP = -TdT,$$

which has an implicit solution given by

$$\int \frac{\epsilon P ln(\frac{P}{P^\circ}) - P\epsilon(P)}{P\epsilon'(P) - \epsilon} dP = -\frac{T^2}{2} + c,$$

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. If $\epsilon(P) = 0$, then $\epsilon'(P) = 0$ and the implicit solutions are given by

$$\int P ln(\frac{P}{P^\circ}) dP = -\frac{T^2}{2} + c,$$

for $c \in \mathcal{R}$. We have, integrating by parts, that

$$\begin{aligned}\int Pln(\frac{P}{P^\circ}) &= \int Pln(P) - Pln(P^\circ)\\ &= \frac{P^2ln(P)}{2} - \int \frac{P}{2} - \frac{P^2ln(P^\circ)}{2}\\ &= \frac{P^2ln(P)}{2} - \frac{P^2}{4} - \frac{P^2ln(P^\circ)}{2}\\ &= P^2(\frac{ln(P)}{2} - \frac{ln(P^\circ)}{2} - \frac{1}{4}),\end{aligned}$$

so that the implicit solutions are given by

$$P^2(\frac{ln(P)}{2} - \frac{ln(P^\circ)}{2} - \frac{1}{4}) + \frac{T^2}{2} = c,$$

for $c \in \mathcal{R}$ as required. The determination of $grad(Q)(T,P)$ when $\epsilon = 0$ is again a simple application of the chain rule. As before, we compute

$$\frac{dP}{dT} = \frac{\frac{-\epsilon'(P)}{RT}e^{\frac{-\epsilon(P)}{RT}}}{\frac{\epsilon(P)}{RT^2}e^{\frac{-\epsilon(P)}{RT}}} = \frac{-\epsilon'(P)T}{\epsilon(P)},$$

so that, separating variables;

$$\frac{\epsilon(P)}{\epsilon'(P)}dP = -TdT,$$

and the implicit solutions are given by

$$\int \frac{\epsilon(P)}{\epsilon'(P)}dP = \frac{-T^2}{2} + c.$$

□

Remark 2. 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.

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 §8.

Lemma 20 (The Nernst equation for the standard cell)**.** *At electrical chemical equilibrium* (T,P) *and* (T,P°)*;*

$$(E - E^\circ)(T,P) = -\frac{RTln(Q(T,P))}{2F} - \frac{\epsilon(P)}{2F}.$$

Proof. For c substances, with c' the number of the charged species, using Definition 1, we have that the electrostatic potential energy;

$$U_{el} = \sum_{i=1}^{c'} \phi(\overline{x}_i)q_i,$$

where $q_i = N_i e z_i = N_A n_i e z_i$ and 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

$$\begin{aligned}G(T,P,n_1,\ldots,n_c) &= U+PV-TS\\&= U_{chem}+U_{el}+PV-TS\\&= U_{el}+G_{chem}\\&= \sum_{j=1}^{c}\phi(\overline{x}_j)q_j+G_{chem}\\&= \sum_{j=1}^{c}\phi(\overline{x}_j)N_An_jez_j+G_{chem},\end{aligned}$$

so that

$$\begin{aligned}\mu_i &= (\frac{\partial G}{\partial n_i})_{T,P}\\&= (\frac{\partial(\sum_{j=1}^{c}\phi(\overline{x}_j)N_An_jez_j+G_{chem})}{\partial n_i})_{T,P}\\&= \mu_{i,chem}, && (c'+1\leq i\leq c)\\&= \mu_{i,chem}+\frac{\partial(\phi(\overline{x}_i)N_An_iez_i)}{\partial n_i}, && (1\leq i\leq c')\\&= \mu_{i,chem}+\phi(\overline{x}_i)N_Aez_i\\&= \mu_{i,chem}+\phi(\overline{x}_i)Fz_i. && (77)\end{aligned}$$

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 5, generalized to a collection involving charged species, using (77), we have that

$$\begin{aligned}(\frac{\partial G}{\partial\xi})_{T,P} &= \textstyle\sum_{i=1}^{c}\nu_i\mu_i\\&= 2\mu(HCl)+2\mu(Ag)-\mu(H_2)-2\mu(AgCl)+2\mu(e^-(L))-2\mu(e^-(R))\\&= (\frac{\partial G_{chem'}}{\partial\xi})_{T,P}+2\mu(e^-(L))-2\mu(e^-(R))\\&= (\frac{\partial G_{chem'}}{\partial\xi})_{T,P}+((2\mu_{chem}(e^-(L))-2F\phi(L))-(2\mu_{chem}(e^-(L))-2F\phi(R)))\\&= (\frac{\partial G_{chem'}}{\partial\xi})_{T,P}+2F(\phi(R)-\phi(L))\\&= (\frac{\partial G_{chem'}}{\partial\xi})_{T,P}+2EF=0, && (78)\end{aligned}$$

where $G_{chem'}$ is the Gibbs energy restricted to the uncharged species. By Lemmas 15 and 16, we have that

$$\begin{aligned}(\frac{\partial G_{chem'}}{\partial\xi})_{T,P^\circ} &= \sum_{i=c'+1}^{c}\nu_i\mu_i^\circ\\&= (\Delta G^\circ_{chem'}+RTln(Q_{chem'}(T,P^\circ))+\epsilon(P^\circ))\\&= (\Delta G^\circ_{chem'}-\epsilon(P^\circ))+\epsilon(P^\circ))\\&= \Delta G^\circ_{chem'}. && (79)\end{aligned}$$

From (78) and (79), we obtain

$$2E^\circ F=-(\frac{\partial G_{chem'}}{\partial\xi})_{T,P^\circ}=-\Delta G^\circ_{chem'}. \tag{80}$$

Similarly, we have that

$$(\frac{\partial G_{chem'}}{\partial \xi})_{T,P} = \sum_{i=c'+1}^{c} \nu_i \mu_i = (\Delta G^{\circ}_{chem'} + RTln(Q_{chem'}(T,P)) + \epsilon(P)), \tag{81}$$

so from (78) and (81), we obtain that

$$2EF = -(\frac{\partial G_{chem'}}{\partial \xi})_{T,P} = -(\Delta G^{\circ}_{chem'} + RTln(Q_{chem'}(T,P)) + \epsilon(P)). \tag{82}$$

Combining (82) and (80), we obtain that

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

so that

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

□

Lemma 21. *At electrical chemical equilibrium (T,P) and (T,P°), and chemical equilibrium (T,P), we have*

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

Proof. By Lemma 20, we have that

$$E - E^{\circ} = -\frac{RTln(Q)}{2F} - \frac{\epsilon(P)}{2F}, \tag{83}$$

and, by Lemma 15, we have that

$$0 = (\frac{\partial G}{\partial \xi})_{T,P} = \Delta G^{\circ} + RTln(Q) + \epsilon(P). \tag{84}$$

Rearranging (83) and (84), we obtain the result. □

Lemma 22. *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 (78) of Lemma 20, we have that

$$(\frac{\partial G}{\partial \xi})_{T,P} = (\frac{\partial G_{chem'}}{\partial \xi})_{T,P} + 2EF. \tag{85}$$

By Lemma 18, we have that $(\frac{\partial G_{chem'}}{\partial \xi})_{T,P}$ is independent of P, in particularly, we have that

$$(\frac{\partial G_{chem'}}{\partial \xi})_{T_1,P_1} = (\frac{\partial G_{chem'}}{\partial \xi})_{T_1,P_1^{\circ}}, \tag{86}$$

so that, combining (85) and (86), we obtain the result. □

Lemma 23. *We have, for all $T_1 > 0, P_1 > 0$, that*

$$2F(E(T_1,P_1) - E^{\circ}(T_1)) = (\frac{\partial G}{\partial \xi})_{T,P}|_{(T_1,P_1)} - (\frac{\partial G}{\partial \xi})_{T,P}|_{(T_1,P_1^{\circ})} - RT_1ln(Q(T_1,P_1)) - \epsilon(P_1).$$

Proof. Following the proof of Lemma 20, we have that

$$(\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1} = (\frac{\partial G_{chem'}}{\partial \xi})_{T,P}|_{T_1,P_1} + 2E(T_1,P_1)F, \tag{87}$$

$$2E^\circ(T_1)F = (\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1^\circ} - (\frac{\partial G_{chem'}}{\partial \xi})_{T,P}|_{T_1,P_1^\circ} = (\frac{\partial G}{\partial \xi})_{T,P}|_{T_1,P_1^\circ} - \Delta G^\circ_{chem'}(T_1), \tag{88}$$

so from (87), (88) and Lemma 15, we have

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

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

□

5. Dilute solutions

Definition 5. As mentioned in Definition 1, we can consider an electrolyte as a solute in a dilute solution. Sometimes the solvent is involved in an electrolytic reaction, for example;

$$2H_2O + 4e^-(R) \rightarrow O_2 + 2H_2 + 4e^-(L), \tag{89}$$

and sometimes not, as in the standard cell, where we can consider H_2O as the solvent not involved in the reaction. In Lemmas 2 to 10, 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

$$\mu_i = \mu_i^\circ + RTln(a_i), \qquad 0 \le i \le c, \tag{90}$$

when we define the activities a_i, for $0 \le i \le c$, which, when (90) holds, involves a contradiction.

Lemma 24. *In Lemmas 2 to 10, 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 $\mu_i = \mu_i^\circ + RTln(a_i)$, $0 \le i \le c$, then, the Lemma 2 reduces to*

$$E - E^\circ = -\frac{RTln(Q)}{2F} + \frac{RTln(\frac{a_0(T,P)}{a_0(T,P^\circ)})}{2F}$$

and Lemma 3 reduces to

$$(\frac{\partial G}{\partial \xi})_{T,P} = \Delta G^\circ + RTln(\frac{Q}{a_0(T,P)})$$

where ΔG° is the Gibbs energy change for 1 mole of reaction without the solvent.

The Lemma 4 reduces to

$$\Delta G^\circ = 2F(E - E^\circ) + RTln(a_0(T,P^\circ)),$$

and Lemma 5 remains 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). Also, chemical equilibrium exists at (T,P) iff $Q(T,P) = a_0 e^{\frac{-\Delta G^\circ}{RT}}$. Moreover, we always have that $Q(T,P^\circ) = 1$.

The Lemma 6 remains 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

$$\begin{aligned} Q(T_2,P) &= e^{\frac{\Delta G^\circ(T_1)-\Delta G^\circ(T_2)}{RT_2}} a_0(T_1,P^\circ)^{\frac{-T_1}{T_2}} a_0(T_2,P), \qquad (91)\\ c &= \Delta G^\circ(T_1) - RT_1 ln(a_0(T_1,P^\circ)),\\ ln(\frac{Q(T_2)}{Q(T_1)}) = ln(Q(T_2)) &= \frac{1}{R}\int_{T_1}^{T_2}\frac{\Delta H^\circ - c}{T^2}dT + ln(\frac{a_0(T_2,P)}{a_0(T_1,P^\circ)}),\\ \frac{\Delta G^\circ(T_2)-\Delta G^\circ(T_1)}{T_2} &= -\int_{T_1}^{T_2}\frac{\Delta H^\circ - c}{T^2}dT + R(1-\frac{T_1}{T_2})ln(a_0(T_1,P^\circ)), \end{aligned}$$

and if ΔH° is temperature independent;

$$\begin{aligned} ln(\frac{Q(T_2)}{Q(T_1)}) = ln(Q(T_2)) &= -(\frac{\Delta H^\circ - c}{R})(\frac{1}{T_2}-\frac{1}{T_1}) + ln(\frac{a_0(T_2,P)}{a_0(T_1,P^\circ)}), \qquad (92)\\ \frac{\Delta G^\circ(T_2)-\Delta G^\circ(T_1)}{T_2} &= (\Delta H^\circ - c)(\frac{1}{T_2}-\frac{1}{T_1}) + R(1-\frac{T_1}{T_2})ln(a_0(T_1,P^\circ)), \qquad (93) \end{aligned}$$

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.

The Lemma 7 remains same with the modification that if $\epsilon \neq 0$; $Q(T_2,P') = e^{\frac{\epsilon ln(\frac{P'}{P'^\circ})}{RT_2}} a_0(T_2,P')$ and the dynamic equilibrium paths are given by $a_0(T_2,P')(\frac{P'}{P'^\circ})^{\frac{\epsilon}{RT_2}} = c$ 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 5, 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 5 go through as before. Going through the proof of Lemma 3, 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 5, 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, 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

$$\begin{aligned} (\frac{\partial G_{chem'}}{\partial \xi})_{T,P^\circ} &= \Delta G^\circ_{chem'} + RTln(Q_{chem'}(T,P^\circ)\\ &= \Delta G^\circ_{chem'} + RTln(\frac{Q}{a_0(T,P^\circ)})\\ &= \Delta G^\circ_{chem'} - RTln(a_0(T,P^\circ)), \qquad (94) \end{aligned}$$

where $G_{chem'}$ is the Gibbs energy restricted to the uncharged species without the solvent. Using (4), from Lemma 2 and (94), we obtain

$$2E^\circ F = -\Delta G^\circ_{chem'} + RTln(a_0(T,P^\circ)). \qquad (95)$$

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 (4), from Lemma 2;

$$2EF = -(\Delta G^{\circ}_{chem'} + RTln(\frac{Q}{a_0(T,P)})). \tag{96}$$

Combining (96) and (91), we obtain

$$\begin{aligned} 2EF - 2E^{\circ}F &= -(\Delta G^{\circ}_{chem'} + RTln(\frac{Q}{a_0(T,P)})) - (-\Delta G^{\circ}_{chem'} + RTln(a_0(T,P^{\circ}))) \\ &= -RTln(\frac{Q}{a_0(T,P)}) - RTln(a_0(T,P^{\circ})) = -RTln(Q) + RTln(\frac{a_0(T,P)}{a_0(T,P^{\circ})}), \end{aligned}$$

which gives the result.of Lemma 2. Going back through the proof of Lemma 5 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 3, 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

$$(\frac{\partial G}{\partial \xi})_{T,P} = \Delta G^{\circ} + RTln(\frac{Q}{a_0(T,P)}) = \Delta G^{\circ} - RTln(a_0(T,P^{\circ})),$$

and

$$(\frac{\partial G}{\partial \xi})_{T,P^{\circ}} = \Delta G^{\circ} + RTln(\frac{Q}{a_0(T,P^{\circ})}) = 0.$$

So that we have chemical equilibrium at (T,P). For the penultimate claim of Lemma 5, rearrange the formula from the modification of Lemma 3, 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 4, we have by the modification of Lemma 2, 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 3, that

$$0 = (\frac{\partial G}{\partial \xi})_{T,P} = \Delta G^{\circ} + RTln(Q) - RTln(a_0(T,P)),$$

so that

$$\begin{aligned} \Delta G^{\circ} &= RTln(a_0(T,P)) - RTln(Q) \\ &= RTln(a_0(T,P)) + 2F(E - E^{\circ}) - RTln(\frac{a_0(T,P)}{a_0(T,P^{\circ})}) \\ &= 2F(E - E^{\circ}) + RTln(a_0(T,P^{\circ})). \end{aligned}$$

For the modification of Lemma 6, 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 5, we have that $Q = a_0 e^{\frac{-\Delta G^\circ}{RT}}$ along a chemical equilibrium path, so that

$$ln(Q) = \frac{-\Delta G^\circ}{RT} + ln(a_0(T,P)). \tag{97}$$

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 (97) and the fundamental theorem of calculus, that

$$\begin{aligned}
ln(\frac{Q(T_2)}{Q(T_1)}) &= ln(Q)(T_2) - ln(Q)(T_1) \\
&= \frac{-\Delta G^\circ(T_2)}{RT_2} + \frac{\Delta G^\circ(T_1)}{RT_1} + ln(a_0(T_2,P_2)) - ln(a_0(T_1,P_1)) \\
&= \int_{T_1}^{T_2} \frac{dln(Q)}{dT} dT \\
&= \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^\circ}{T^2} + \int_{T_1}^{T_2} \frac{d}{dT}(ln(a_0(T,P)))dT \\
&= \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^\circ}{T^2} + ln(a_0(T_2,P_2)) - ln(a_0(T_1,P_1)).
\end{aligned} \tag{98}$$

So that, rearranging, we obtain the first claim. Using the fact, by the modification of Lemma 3, that

$$\begin{aligned}
ln(Q(T_2)) &= -\frac{\Delta G^\circ(T_2)}{RT_2} + ln(a_0(T_2,P_2)), \\
ln(Q(T_1)) &= -\frac{\Delta G^\circ(T_1)}{RT_1} + ln(a_0(T_1,P_1)).
\end{aligned}$$

We obtain, substituting into (98), canceling R, and performing the integration, if ΔH° is temperature independent, that

$$\frac{\Delta G^\circ(T_2)}{T_2} - \frac{\Delta G^\circ(T_1)}{T_1} = -\int_{T_1}^{T_2} \frac{\Delta H^\circ}{T^2} = \Delta H^\circ(\frac{1}{T_2} - \frac{1}{T_1}). \tag{99}$$

For the fifth claim, rearrange (99). If D_c intersects the line $P = P^\circ$ at (T_1, P°), for the sixth and seventh claims, we have, using the modification of Lemma 3 and the fact from Lemma 5 that $Q(T_1, P^\circ) = 1$;

$$\begin{aligned}
(\frac{\partial G}{\partial \xi})_{T_2,P} &= \Delta G^\circ(T_2) + RT_2 ln(Q(T_2,P)) - RT_2 ln(a_0(T_2,P)) \\
&= (\frac{\partial G}{\partial \xi})_{T_1,P^\circ} \\
&= \Delta G^\circ(T_1) + RT_1 ln(Q(T_1,P^\circ)) - RT_1 ln(a_0(T_1,P^\circ)) \\
&= \Delta G^\circ(T_1) - RT_1 ln(a_0(T_1,P^\circ)) = c.
\end{aligned}$$

So that, again rearranging, we obtain the result. Along D_c, we have, using Lemma 3, that

$$ln(Q) = \frac{c - \Delta G^\circ}{RT} + ln(a_0(T,P)),$$

so that, using the first part;

$$\begin{aligned}
\frac{dln(Q)}{dT} &= \frac{d}{dT}(\frac{c - \Delta G^\circ}{RT}) + \frac{d}{dT}(ln(a_0(T,P))) \\
&= \frac{-c}{RT^2} + \frac{d}{dT}(\frac{-\Delta G^\circ}{RT}) + \frac{d}{dT}(ln(a_0(T,P))) \\
&= \frac{\Delta H^\circ - c}{RT^2} + \frac{d}{dT}(ln(a_0(T,P))),
\end{aligned}$$

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 3;

$$\begin{aligned} ln(Q(T_2)) &= \frac{c - \Delta G^\circ(T_2)}{RT_2} + ln(a_0(T_2, P)), \\ ln(Q(T_1)) &= 0, \end{aligned}$$

so that, using the formula for c;

$$\begin{aligned} ln(Q(T_2)) &= ln(Q(T_2)) - ln(Q(T_1)) \\ &= \frac{c - \Delta G^\circ(T_2)}{RT_2} + ln(a_0(T_2, P)) \\ &= \frac{\Delta G^\circ(T_1) - RT_1 ln(a_0(T_1, P^\circ)) - \Delta G^\circ(T_2)}{RT_2} + ln(a_0(T_2, P)) \\ &= \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^\circ - c}{T^2} dT + ln(a_0(T_2, P_2)) - ln(a_0(T_1, P^\circ)) \\ &= \frac{-1}{R}(\Delta H^\circ - c)(\frac{1}{T_2} - \frac{1}{T_1}) + ln(a_0(T_2, P_2)) - ln(a_0(T_1, P^\circ)), \end{aligned}$$

and rearranging;

$$\begin{aligned} \frac{\Delta G^\circ(T_1) - RT_1 ln(a_0(T_1, P^\circ)) - \Delta G^\circ(T_2)}{RT_2} &= \frac{-1}{R}(\Delta H^\circ - c)(\frac{1}{T_2} - \frac{1}{T_1}) - ln(a_0(T_1, P^\circ)), \\ \frac{\Delta G^\circ(T_2) - \Delta G^\circ(T_1)}{T_2} + \frac{RT_1 ln(a_0(T_1, P^\circ))}{T_2} &= (\Delta H^\circ - c)(\frac{1}{T_2} - \frac{1}{T_1}) + Rln(a_0(T_1, P^\circ)), \end{aligned}$$

$$\begin{aligned} \frac{\Delta G^\circ(T_2) - \Delta G^\circ(T_1)}{T_2} &= (\Delta H^\circ - c)(\frac{1}{T_2} - \frac{1}{T_1}) + Rln(a_0(T_1, P^\circ)) - \frac{RT_1 ln(a_0(T_1, P^\circ))}{T_2} \\ &= (\Delta H^\circ - (\Delta G^\circ(T_1) - RT_1 ln(a_0(T_1, P^\circ))))(\frac{1}{T_2} - \frac{1}{T_1}) + Rln(a_0(T_1, P^\circ)) - \frac{RT_1 ln(a_0(T_1, P^\circ))}{T_2} \\ &= (\Delta H^\circ - \Delta G^\circ(T_1))(\frac{1}{T_2} - \frac{1}{T_1}) + RT_1 ln(a_0(T_1, P^\circ))(\frac{1}{T_2} - \frac{1}{T_1}) + (R - \frac{RT_1}{T_2}) ln(a_0(T_1, P^\circ)) \\ &= (\Delta H^\circ - \Delta G^\circ(T_1))(\frac{1}{T_2} - \frac{1}{T_1}) + ln(a_0(T_1, P^\circ))(RT_1(\frac{1}{T_2} - \frac{1}{T_1}) + (R - \frac{RT_1}{T_2})) \\ &= (\Delta H^\circ - \Delta G^\circ(T_1))(\frac{1}{T_2} - \frac{1}{T_1}), \end{aligned}$$

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 7, 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 3, to obtain the formula for the activity coefficient;

$$Q(T_2, P') = e^{\frac{(\frac{\partial G}{\partial \xi})_{T,P}|_{T_2,P'} - \Delta G^{\circ}(T_2) + RT_2 ln(a_0(T_2,P'))}{RT_2}} = e^{\frac{\epsilon ln(\frac{P'}{P'^{\circ}})}{RT_2}} a_0(T_2, P').$$

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. $\square$

Lemma 25. *In Lemmas 2 to 10, for the case of a reaction like (89) in Definition 5, 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.*

Remark 3. 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 11 and 13. This is done in Lemma 44. For the existence of a feasible path, where we require that the n_0 term is fixed, see Remark 5, we need to change Lemma 12. Letting $d_0 > 0$ denote the fixed molar amount of the solvent, we obtain the relation, modifying the proof of Lemma 12;

$$d_0 \prod_{i=1}^{c-1} (\frac{\nu_i}{\nu_c} n_c + d_i)^{\nu_i}(t) n_c^{\nu_c}(t) = \epsilon(t)((\sum_{i=1}^{c-1} \frac{\nu_i}{\nu_c} + 1) n_c + \sum_{i=0}^{c-1} d_i)^{w}(t),$$

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 12, 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. As mentioned in Definition 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

$$\begin{aligned} a_0 &= x_0 \simeq 1, \\ a_i &= x_i, \qquad\qquad (1 \leq i \leq c), \end{aligned}$$

and define

$$\begin{aligned} Q &= a_0 \prod_{i=1}^{c} a_i^{\nu_i} \simeq \prod_{i=1}^{c} a_i^{\nu_i}, \qquad \text{(no interaction of the solvent)} \\ Q &= \prod_{i=0}^{c} a_i^{\nu_i}, \qquad \text{(interaction of the solvent)}, \end{aligned}$$

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;

$$\mu_i^{(sol)} = \mu_i^{(g)\circ} + RTln(\frac{P_i}{P^{\circ}}) = \mu_i^{(g)\circ} + RTln(\frac{k_i x_i}{P^{\circ}}) = \mu_i^{(H)\circ} + RTln(x_i), \tag{100}$$

where

$$\mu_i^{(H)\circ} = \mu_i^{(g)\circ} + RTln(\frac{k_i}{P^{\circ}}). \tag{101}$$

From (100), we obtain that

$$\mu_i^\circ = \mu_i^{(H)\circ} + RTln(x_i(T,P^\circ)), \tag{102}$$

and, for $1 \leq i \leq c$;

$$\mu_i = \mu_i^\circ - RTln(x_i(T,P^\circ)) + RTln(x_i) = \mu_i^\circ + RTln(x_i) + \kappa(T), \tag{103}$$

where, from phase equilibrium and (101) and (102);

$$\kappa(T) = -RTln(x_i(T,P^\circ)) = \mu_i^{(H)\circ} - \mu_i^\circ = \mu_i^{(g)\circ} + RTln(\frac{k_i}{P^\circ}) - \mu_i^{(sol)\circ} = RTln(\frac{k_i}{P^\circ}).$$

We can use Raoult's law for the solvent as $P_0 = P_0^* x_0$, see [7]. Then, using equilibrium with an ideal gas mixture;

$$\begin{aligned}
&\mu_0^{(sol)} = \mu_0^{\circ(g)} + RTln(\frac{P_0}{P^\circ}) = \mu_0^{\circ(g)} + RTln(\frac{P_0^* x_0}{P^\circ}),\\
&\mu_0^{\circ(g)} + RTln(x_0) + RTln(\frac{P_0^*}{P^\circ}) = \mu_0^*(T,P_0^*) + RTln(x_0) = \mu_0^*(T,P) + RTln(x_0) + \theta(T,P),
\end{aligned} \tag{104}$$

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

$$\mu_0 = \mu_0^* + RTln(x_0) + \theta = \mu_0^* + RTln(\frac{P_0}{P^\circ}) - RTln(\frac{P_0^*}{P^\circ}) + \theta. \tag{105}$$

We also have, using the phase rule for the solvent in equilibrium with an ideal gas mixture, that

$$\begin{aligned}
\mu_0^{(g)} &= \mu_0^{\circ(g)} + RTln(\frac{P_0}{P^\circ}),\\
\mu_0^{(sol)} &= \mu_0^{\circ(sol)} + RTln(\frac{P_0}{P^\circ}).
\end{aligned} \tag{106}$$

Combining (106) and (105), we obtain that

$$\begin{aligned}
\mu_0^* &= \mu_0 - RTln(\frac{P_0}{P^\circ}) + RTln(\frac{P_0^*}{P^\circ}) - \theta\\
&= (\mu_0^\circ + RTln(\frac{P_0}{P^\circ})) - RTln(\frac{P_0}{P^\circ}) + RTln(\frac{P_0^*}{P^\circ}) - \theta\\
&= \mu_0^\circ + RTln(\frac{P_0^*}{P^\circ}) - \theta.
\end{aligned} \tag{107}$$

Letting $P_0^* = P^\circ$, we obtain that $\mu_0^*(T,P') = \mu_0^\circ - \theta$, for the corresponding P', (105).

From (104) and (105), we obtain that

$$\begin{aligned}
\mu_0 &= \mu_0^* + RTln(x_0) + \theta\\
&= \mu_0^*(T,P') + \delta + RTln(x_0) + \theta\\
&= \mu_0^\circ - \theta + \delta + RTln(x_0) + \theta\\
&= \mu_0^\circ + RTln(x_0) + \delta,
\end{aligned}$$

where $\delta = \mu_0^*(T,P) - \mu_0^*(T,P') \simeq 0$.

Using the same calculation as before, we have that

$$\mu_0 = \mu_0^\circ + RTln(x_0) + \gamma(P).$$

Lemma 26. *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 11, as we are differentiating, the proof works with a constant $f > 0$. □

We reformulate Lemmas 15 to 19 in this context, assuming Henry's law for the solutes and the solvent an ideal solution.

Lemma 27. *In the dilute solution case, with interaction of the solvent, for the energy function G involving* $c + 1$ *uncharged species;*

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

where $\epsilon(T, P) = \nu_0\gamma_0(P) + \sum_{i=1}^{c} \nu_i\kappa_i(T) \simeq 0$, $\gamma_0(P) \simeq 0$ *and* $\kappa_i(T) \simeq 0$ *are the error term for the i'th uncharged species in Definition 6,* $1 \leq i \leq c$.

Proof. The proof is clear from Lemma 15. □

Lemma 28. *For a dilute solution, with interaction of the solvent, we have, using the definition of* $\epsilon(T, P)$ *in Lemma 27, the error term* $\gamma_0(P)$ *and the error terms* $\kappa_i(T)$, $1 \leq i \leq c$ *in Definition 5, that the same results as Lemma 16 hold, replacing* $\epsilon(P)$ *with* $\epsilon(T, P)$ *and* δ *with* $\epsilon(T, P^\circ) = \nu_0\gamma_0(P^\circ) + \sum_{i=1}^{c} \nu_i\kappa_i(T)$.

Proof. The proof is clear from the proof of Lemma 16. □

Lemma 29. *For a dilute solution, with interaction of the solvent, we have the same result as Lemma 17 hold, replacing* $\epsilon(P(T))$ *by* $\epsilon(T, P(T))$ *along the quasi-chemical equilibrium lines.*

Proof. The proof is clear from the proof of Lemma 17. □

Lemma 30. *For a dilute solution, with interaction of the solvent, we have the same results as Lemma 18 hold, replacing* $\epsilon(P')$ *by* $\epsilon(T_1, P')$*. In particularly, if* $\epsilon \neq 0$*, we have that*

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

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 18. □

Lemma 31. *For a dilute solution, with interaction of the solvent, we have that, if* $\epsilon \neq 0$*;*

$$grad(Q)(T, P) = ((\frac{-\epsilon ln(\frac{P}{P^\circ})}{RT^2} + \frac{\epsilon(T, P)}{RT^2} - \frac{\frac{\partial \epsilon}{\partial T}(T, P)}{RT})(\frac{P}{P^\circ})^{\frac{\epsilon}{RT}} e^{\frac{-\epsilon(T,P)}{RT}}, (\frac{\epsilon P^\circ}{RTP} - \frac{\frac{\partial \epsilon}{\partial P}(T, P)}{RT})(\frac{P}{P^\circ})^{\frac{\epsilon}{RT}} e^{\frac{-\epsilon(T,P)}{RT}}),$$

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;

$$\begin{aligned}\frac{dP}{dT} &= \frac{\epsilon TP^\circ - PT\frac{\partial\epsilon}{\partial P}(T,P)}{(-\epsilon Pln(\frac{P}{P^\circ}) + P\epsilon(T,P) - PT\frac{\partial\epsilon}{\partial T}(T,P))},\\ \frac{dP}{dT} &= \frac{-T\frac{\partial\epsilon}{\partial P}(T,P)}{\epsilon(T,P) - T\frac{\partial\epsilon}{\partial T}(T,P)},\end{aligned}$$

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 19, noting the claim about maximal reaction is still valid with the same definition of Q, if $\epsilon \neq 0$, we compute

$$\frac{dP}{dT} = \frac{(\frac{\epsilon P^\circ}{RTP} - \frac{\frac{\partial\epsilon}{\partial P}(T,P)}{RT})(\frac{P}{P^\circ})^{\frac{\epsilon}{RT}} e^{\frac{-\epsilon(T,P)}{RT}}}{(\frac{-\epsilon ln(\frac{P}{P^\circ})}{RT^2} + \frac{\epsilon(T,P)}{RT^2} - \frac{\frac{\partial\epsilon}{\partial T}(T,P)}{RT})(\frac{P}{P^\circ})^{\frac{\epsilon}{RT}} e^{\frac{-\epsilon(T,P)}{RT}}} = \frac{\epsilon TP^\circ - PT\frac{\partial\epsilon}{\partial P}(T,P)}{(-\epsilon Pln(\frac{P}{P^\circ}) + P\epsilon(T,P) - PT\frac{\partial\epsilon}{\partial T}(T,P))},$$

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. Dilute solutions with Fugacity and interaction of the solvent

Definition 7. As mentioned in Definition 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;

$$\begin{aligned}a_0 &= \gamma_0 x_0 \simeq 1,\\ a_i &= \gamma_i x_i, \qquad 1 \leq i \leq c.\end{aligned}$$

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 [7], so that, by the approximation of Henry's Law, phase equilibrium and the gas law with fugacity δ_i;

$$\begin{aligned}\mu_i^{(sol)} &= \mu_i^{(g)\circ} + RTln(\frac{\delta_i P_i}{P^\circ})\\ &= \mu_i^{(g)\circ} + RTln(\frac{k_i x_i \gamma_i}{P^\circ}) + RTln(\delta_i(T,P))\\ &= \mu_i^{(H)\circ} + RTln(\gamma_i x_i) + RTln(\delta_i(T,P)), \qquad (108)\end{aligned}$$

where

$$\mu_i^{(H)\circ} = \mu_i^{(g)\circ} + RTln(\frac{k_i}{P^\circ}). \qquad (109)$$

From (108), we obtain that;

$$\mu_i^\circ = \mu_i^{(H)\circ} + RTln(\gamma_i x_i(T,P^\circ)) + RTln(\delta_i(T,P^\circ)), \qquad (110)$$

and, for $1 \leq i \leq c$;

$$\mu_i = \mu_i^\circ - RTln(\gamma_i x_i(T,P^\circ)) - RTln(\delta_i(T,P^\circ) + RTln(\gamma_i x_i) + RTln(\delta_i(T,P)) = \mu_i^\circ + RTln(\gamma_i x_i) + \kappa(T,P), \qquad (111)$$

where, from phase equilibrium and (109) and (110);

$$\begin{aligned}\kappa(T,P) &= -RTln(\gamma_i x_i(T,P^\circ)) + RT(ln(\delta_i(T,P)) - ln(\delta_i(T,P^\circ)) \\ &= \mu_i^{(H)\circ} - \mu_i^\circ + RTln(\delta_i(T,P^\circ)) + RTln(\frac{\delta_i(T,P)}{\delta_i(T,P^\circ)}) \\ &= \mu_i^{(g)\circ} + RTln(\frac{k_i}{P^\circ}) - \mu_i^{(sol)\circ} + RTln(\delta_i(T,P)) \\ &= RTln(\frac{k_i}{P^\circ}) + RTln(\delta_i(T,P)) \\ &= RTln(\frac{k_i\delta_i(T,P)}{P^\circ}).\end{aligned}$$

We can measure the correction in Raoult's law for the solvent by $P_0 = \gamma_0 P_0^* x_0$, (convention I), see [7]. 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

$$\mu_0^{(sol)} = \mu_0^{\circ(g)} + RTln(\frac{\delta_0 P_0}{P^\circ}) = \mu_0^{\circ(g)} + RTln(\frac{\delta_0\gamma_0 P_0^* x_0}{P^\circ}),$$

$$\begin{aligned}\mu_0^{\circ(g)} + RTln(\gamma_0 x_0) + RTln(\frac{\delta_0 P_0^*}{P^\circ}) &= \mu_0(T,P_0^*) + RTln(\gamma_0 x_0) \\ &= \mu_0^*(T,P_0^*) + \sigma(T,P_0^*) + RTln(\gamma_0 x_0) \\ &= \mu_0^*(T,P) + RTln(\gamma_0 x_0) + \theta(T,P), \end{aligned} \tag{112}$$

where $\theta(T,P) = \mu_0^*(T,P_0^*) - \mu_0^*(T,P) + \sigma(T,P_0^*)$, so that

$$RTln(\gamma_(0)x_0) = RTln(\frac{\delta_0 P_0}{P^\circ}) - RTln(\frac{\delta_0 P_0^*}{P^\circ}),$$

and

$$\mu_0 = \mu_0^* + RTln(\gamma_0 x_0) + \theta = \mu_0^* + RTln(\frac{\delta_0 P_0}{P^\circ}) - RTln(\frac{\delta_0 P_0^*}{P^\circ}) + \theta. \tag{113}$$

We also have, using the phase rule for the solvent in equilibrium, that

$$\begin{aligned}\mu_0^{(g)} &= \mu_0^{\circ(g)} + RTln(\frac{\delta_0 P_0}{P^\circ}), \\ \mu_0^{(sol)} &= \mu_0^{\circ(sol)} + RTln(\frac{\delta_0 P_0}{P^\circ}).\end{aligned} \tag{114}$$

Combining (114) and (113), we obtain that

$$\begin{aligned}\mu_0^* &= \mu_0 - RTln(\frac{\delta_0 P_0}{P^\circ}) + RTln(\frac{\delta_0 P_0^*}{P^\circ}) - \theta \\ &= (\mu_0^\circ + RTln(\frac{\delta_0 P_0}{P^\circ})) - RTln(\frac{\delta_0 P_0}{P^\circ}) + RTln(\frac{\delta_0 P_0^*}{P^\circ}) - \theta \\ &= \mu_0^\circ + RTln(\frac{\delta_0 P_0^*}{P^\circ}) - \theta.\end{aligned} \tag{115}$$

Letting $\delta_0 P_0^* = P^\circ$, we obtain that $\mu_0^*(T,P') = \mu_0^\circ - \theta$, for the corresponding P', (113).

From (112) and (113), we obtain that

$$\begin{aligned}\mu_0 &= \mu_0^* + RTln(\gamma_0 x_0) + \theta \\ &= \mu_0^*(T,P') + \delta + RTln(\gamma_0 x_0) + \theta \\ &= \mu_0^\circ - \theta + \delta + RTln(\gamma_0 x_0) + \theta \\ &= \mu_0^\circ + RTln(\gamma_0 x_0) + \delta,\end{aligned}$$

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

$$\begin{aligned} b_0 &= x_0, \\ b_i &= x_i, \qquad\qquad 1 \leq i \leq c. \end{aligned}$$

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 32. *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 26. □

We reformulate Lemmas 15 to 19 in this context, assuming the approximation to Henry's law for the solutes and the approximation to Raoult's law for the solvent.

Lemma 33. *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 7, and ψ_i, for $1 \leq i \leq c$ are the error terms for the solutes in Definition 7.

Proof. The proof is clear from Lemma 15. □

Lemma 34. *For a dilute solution, with interaction of the solvent, we have, using the definition of $\epsilon(T,P)$ in Lemma 33, the error term $\phi_0(T,P)$ and the error terms $\psi_i(T,P)$, $1 \leq i \leq c$ in Definition 7, that the same results as Lemma 16 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 16. □

Lemma 35. *For a dilute solution, with interaction of the solvent, we have the same result as Lemma 17 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 17 □

Lemma 36. *For a dilute solution, with interaction of the solvent, we have the same results as Lemma 18 hold, replacing $\epsilon(P')$ by $\epsilon(T_1,P')$. In particularly, if $\epsilon \neq 0$, we have that*

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

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 18. □

Lemma 37. *For a dilute solution, with interaction of the solvent, we have that, if* $\epsilon \neq 0$*;*

$$grad(Z)(T,P) = ((\frac{-\epsilon ln(\frac{P}{P^\circ})}{RT^2} + \frac{\epsilon(T,P)}{RT^2} - \frac{\frac{\partial\epsilon}{\partial T}(T,P)}{RT})(\frac{P}{P^\circ})^{\frac{\epsilon}{RT}} e^{\frac{-\epsilon(T,P)}{RT}}, (\frac{\epsilon P^\circ}{RTP} - \frac{\frac{\partial\epsilon}{\partial P}(T,P)}{RT})(\frac{P}{P^\circ})^{\frac{\epsilon}{RT}} e^{\frac{-\epsilon(T,P)}{RT}}),$$

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;*

$$\frac{dP}{dT} = \frac{\epsilon TP^\circ - PT\frac{\partial\epsilon}{\partial P}(T,P)}{(-\epsilon Pln(\frac{P}{P^\circ}) + P\epsilon(T,P) - PT\frac{\partial\epsilon}{\partial T}(T,P))},$$
$$\frac{dP}{dT} = \frac{-T\frac{\partial\epsilon}{\partial P}(T,P)}{\epsilon(T,P) - T\frac{\partial\epsilon}{\partial T}(T,P)}.$$

respectively.

Proof. The proof is the same as Lemma 31, replacing Q by Z, noting that Z is defined the same way in terms of activities. □

8. 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 7, we have the following results;

Lemma 38 (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 20, replacing $\epsilon(P)$ with $\epsilon(T,P)$ and use the fact that the catalyzer reaction $2H_2O + 4e^-(R) \rightarrow O_2 + 2H_2 + 4e^-(L)$ occurs with 4 electrons rather than 2. □

Lemma 39. *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 21, replacing $\epsilon(P)$ with $\epsilon(T,P)$, noting the remark in Lemma 38. □

Lemma 40. *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 22, replacing the result there that $(\frac{\partial G_{chem'}}{\partial\xi})_{T,P}$ is independent of P, with the corresponding same result in Lemma 36. □

Lemma 41. *We have, for all* $T_1 > 0, P_1 > 0$*, that*

$$4F(E(T_1,P_1) - E^\circ(T_1)) = (\frac{\partial G}{\partial\xi})_{T,P}|_{(T_1,P_1)} - (\frac{\partial G}{\partial\xi})_{T,P}|_{(T_1,P_1^\circ)} - RT_1ln(Z(T_1,P_1)) - \epsilon(T_1,P_1). \qquad (116)$$

Proof. Follow the proof of Lemma 23, replacing $\epsilon(P)$ with $\epsilon(T,P)$.
$\square$

Remark 4. The result of Lemma 41 combined with the determination of the activity coefficient Z in Lemma 36 and the error term $\epsilon(T,P)$ in Lemma 33 can be use to determine the unknown quantity $(\frac{\partial \mathcal{G}}{\partial \xi})_{T,P}$. We can measure the potential difference between the cathode and anode along the dynamical equilibrium paths provided by Lemma 36 and then use the formula (116) in Lemma 41. Once this is determined, we then alter the power supply, in accordance with (116), to push the reaction along the paths of maximal reaction given in Lemma 37. This should improve the efficiency of the production of hydrogen and oxygen, in the case of the electrolyzer reaction, given by $2H_2O + 4e^-(R) \rightarrow O_2 + 2H_2 + 4e^-(L)$.

9. Dilute solutions with Henry's law for solutes, Raoult's law for the solvent and no solvent interaction

As mentioned in Definition 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

$$\begin{aligned} a_0 &= x_0 \simeq 1, \\ a_i &= x_i, && 1 \leq i \leq c. \end{aligned}$$

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.

Remark 5. 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 $\gamma : [0,1] \rightarrow \mathcal{R}_{>0}^{3+c}$, 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 12, where we are free to take any $n_0 > 0$.

Lemma 42. *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

$$W = \prod_{i=1}^{c} a_i^{\nu_i} = \prod_{i=1}^{c} x_i^{\nu_i} = f. \tag{117}$$

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 11, 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 13, using the additional fact that $n_0' = 0$. $\square$

Lemma 43. *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 11 again, getting the other directions from Lemma 13. $\square$

Lemma 44. *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 43, we have that

$$a_0\prod_{i=1}^{c}a_i^{\nu_i}=x_0\prod_{i=1}^{c}x_i^{\nu_i}=\prod_{i=0}^{c}x_i^{\mu_i}=Q=f, \tag{118}$$

where $x_i=\frac{n_i}{n}$, $\mu_0=1$, $\mu_i=\nu_i$, $1\leq i\leq c$. Now, using the relation (118), differentiating and using the facts that, for $1\leq i\leq c-1$; $n_i'=\frac{\mu_i n_c'}{\mu_c}$, $n_i=\frac{\mu_i n_c}{\mu_c}+d_i$, $n_0'=0$ and $n_0=d_0$, 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

$$\begin{aligned}\sum_{i=0}^{c}\mu_i\frac{n}{n_i}\frac{(n_i'n-n_in')}{n^2}&=\sum_{i=0}^{c}\mu_i(\frac{n_i'}{n_i}-\frac{n'}{n})\\&=\sum_{i=1}^{c-1}\frac{\mu_i^2n_c'}{\nu_in_c+\mu_cd_i}+\frac{\mu_cn_c'}{n_c}-\lambda(\frac{\sum_{i=0}^{c}n_i'}{\sum_{i=0}^{c}n_i})\\&=\sum_{i=1}^{c-1}\frac{\mu_i^2n_c'}{\mu_in_c+\mu_cd_i}+\frac{\mu_cn_c'}{n_c}-\lambda(\frac{(\sum_{i=1}^{c-1}\frac{\mu_i}{\mu_c}+1)n_c'}{(\sum_{i=1}^{c-1}\frac{\nu_i}{\nu_c}+1)n_c+\sum_{i=0}^{c-1}d_i})\\&=0,\end{aligned} \tag{119}$$

where $\lambda=\sum_{i=0}^{c}\mu_i=1+\sum_{i=1}^{c}\nu_i$.

Following the proof of Lemma 11, 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 11, if $n_c'\neq 0$, we obtain the relation;

$$\sum_{i=1}^{c-1}\frac{\mu_i^2}{\mu_in_c+\mu_cd_i}+\frac{\mu_c}{n_c}=\sum_{i=1}^{c-1}\frac{\nu_i^2}{\nu_in_c+\nu_cd_i}+\frac{\nu_c}{n_c}=0,$$

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 11, we can assume this choosing the appropriate pivot. The other directions in the Lemma follow from a simple modification of Lemma 13. ☐

Lemma 45. *In Lemmas 2 to 10, for the standard cell, and considering a dilute solution with no interaction of the solvent, replacing Q defined as* $\prod_{i=1}^{c}a_i^{\nu_i}$ *and with 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 24, 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 46. *In Lemmas 2 to 10, 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* $a_0(\prod_{i=1}^{c}a_i^{\nu_i})=x_0(\prod_{i=1}^{c}a_i^{\nu_i})$ *and 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 24, with the new definition of* $a_0(T,P)=x_0(T,P)$.

Proof. The proof is clear. ☐

In this context, assuming Henry's law for the solutes and the solvent an ideal solution, we reformulate Lemmas 15 to 19.

Lemma 47. *In the dilute solution case, with no interaction of the solvent, for the energy function G involving* $c+1$ *uncharged species, including the solvent, we have*

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

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,* $1\leq i\leq c$.

Proof. The proof is clear from Lemma 15 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 48. *For a dilute solution, with no interaction of the solvent, 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, the same results as Lemma 16 hold, replacing* $\epsilon(P)$ *with* $\epsilon(T)$ *and* δ *with* $\epsilon(T)=\sum_{i=1}^{c}\nu_i\kappa_i(T)$ *and using W instead of Q.*

Proof. The proof is clear from the proof of Lemma 16 and using the observation from Lemma 47.
□

Lemma 49. *For a dilute solution, with no interaction of the solvent, the same result as Lemma 17 holds, 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 17.
□

Lemma 50. *For a dilute solution, with no interaction of the solvent, the same results as Lemma 18 hold, replacing* $\epsilon(P')$ *by* $\epsilon(T_1)$*. In particularly, if* $\epsilon\neq 0$*, we have* $W(T,P)=e^{\frac{\epsilon ln(\frac{P}{P^\circ})-\epsilon(T)}{RT}}$*, and, if* $\epsilon=0$*, we have* $W(T,P)=e^{\frac{-\epsilon(T)}{RT}}$.

Proof. The proof is clear from the proof of Lemma 18.
□

Lemma 51. *For a dilute solution, with no interaction of the solvent, we have that, if* $\epsilon\neq 0$;

$$grad(W)(T,P)=((\frac{-\epsilon ln(\frac{P}{P^\circ})}{RT^2}+\frac{\epsilon(T)}{RT^2}-\frac{\frac{d\epsilon}{dT}(T)}{RT})(\frac{P}{P^\circ})^{\frac{\epsilon}{RT}}e^{\frac{-\epsilon(T)}{RT}},(\frac{\epsilon P^\circ}{RTP})(\frac{P}{P^\circ})^{\frac{\epsilon}{RT}}e^{\frac{-\epsilon(T)}{RT}}),$$

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;*

$$\frac{dP}{dT}=\frac{\epsilon TP^\circ}{(-\epsilon Pln(\frac{P}{P^\circ})+P\epsilon(T)-PT\frac{d\epsilon}{dT}(T))}$$
$$\frac{dP}{dT}=0,$$

respectively.

Proof. The computation follows easily from the proof of Lemma 31, replacing $\epsilon(P,T)$ by $\epsilon(T)$. We also note that in the proof of maximal reaction, see Lemma 19, 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 remains unchanged. □

Remark 6. We can also formulate versions of Lemmas 47 to 51 for the activity coefficient Q instead of W, mentioned in the introduction to the §9. However, although the proof should go through, it is more difficult, and left as an exercise for the reader, combining the methods of §3 and §5. However, it seems unnecessary when we can derive the main results with the coefficient W.

10. Dilute solutions with Fugacity and no solvent interaction

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

$$\begin{aligned} b_0 &= x_0, \\ b_i &= x_i, \qquad\qquad 1 \leq i \leq c. \end{aligned}$$

We refer to the introductions of §7 and §9 with the Remark 5. We will again consider both cases.

Lemma 52. *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. The proof is similar to the proof of Lemma 42. □

Lemma 53. *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

$$\prod_{i=1}^{c} b_i^{\nu_i} = \frac{Z}{b_0} = \prod_{i=1}^{c} x_i^{\nu_i} = \frac{f}{b_0} = d.$$

The remaining proof is similar to the proof of Lemma 43. □

Lemma 54. *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

$$b_0 \prod_{i=1}^{c} b_i^{\nu_i} = x_0 \prod_{i=1}^{c} x_i^{\nu_i} = Z = f.$$

The remaining proof is similar to the proof of Lemma 44. □

Lemma 55. *In Lemmas 2 to 10, 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 definition of W, and assuming without approximation that* $\mu_i = \mu_i^{\circ} + RTln(b_i)$, $1 \leq i \leq c$, *then the same results as Lemma 24 can be obtained by setting* $a_0(T,P) = 1$, *with the same caveat as Lemma 45.*

Proof. The proof follows from the proof of the Lemma 45. □

Lemma 56. *In Lemmas 2 to 10, 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* $Z = b_0(\prod_{i=1}^{c} b_i^{\nu_i}) = x_0(\prod_{i=1}^{c} b_i^{\nu_i})$ *and assuming without approximation that* $\mu_i = \mu_i^{\circ} + RTln(b_i)$, $0 \leq i \leq c$, *then the same results as Lemma 24 can be obtained with the new definition of* $b_0(T,P) = x_0(T,P)$ *replacing* $a_0(T,P)$ *in the Lemma 46.*

Proof. The proof follows from the proof of the Lemma 46. □

In this context, assuming the approximation to Henry's law for the solutes and the approximation to Raoult's law for the solvent, we reformulate Lemmas 15 to 19.

Lemma 57. *In the dilute solution case, with no interaction of the solvent, for the energy function G involving* $c+1$ *uncharged species, we have*

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

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 7.*

Proof. The proof is clear from Lemma 15, with the same observation as in Lemma 47.
□

Lemma 58. *For a dilute solution, with no interaction of the solvent, using the definition of $\epsilon(T,P)$ in Lemma 57 and the error terms $\psi_i(T,P)$, $1 \leq i \leq c$ in Definition 7, the same results as Lemma 16 hold, replacing $\epsilon(P)$ with $\epsilon(T,P)$ and δ with $\epsilon(T,P^\circ) = \sum_{i=1}^{c} \nu_i \psi_i(T,P^\circ)$ and using W instead of Q.*

Proof. The proof is clear from the proof of Lemma 16 and Lemma 57. □

Lemma 59. *For a dilute solution, with no interaction of the solvent, the same results as Lemma 17 hold, replacing $\epsilon(P(T))$ by $\epsilon(T,P(T))$ along the quasi-chemical equilibrium lines.*

Proof. The proof is clear from the proof of Lemma 17 and Lemma 58. □

Lemma 60. *For a dilute solution, with no interaction of the solvent, the same results as Lemma 18 hold, replacing $\epsilon(P')$ by $\epsilon(T_1,P')$. In particularly, if $\epsilon \neq 0$, we have that*

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

and, if $\epsilon = 0$, we have that

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

Proof. The proof is clear from the proof of Lemma 18 and Lemma 59. □

Lemma 61. *For a dilute solution, with no interaction of the solvent, we have that, if $\epsilon \neq 0$;*

$$grad(W)(T,P) = ((\frac{-\epsilon ln(\frac{P}{P^\circ})}{RT^2} + \frac{\epsilon(T,P)}{RT^2} - \frac{\frac{\partial \epsilon}{\partial T}(T,P)}{RT})(\frac{P}{P^\circ})^{\frac{\epsilon}{RT}} e^{\frac{-\epsilon(T,P)}{RT}}, (\frac{\epsilon P^\circ}{RTP} - \frac{\frac{\partial \epsilon}{\partial P}(T,P)}{RT})(\frac{P}{P^\circ})^{\frac{\epsilon}{RT}} e^{\frac{-\epsilon(T,P)}{RT}}),$$

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;

$$\frac{dP}{dT} = \frac{\epsilon T P^\circ - PT\frac{\partial \epsilon}{\partial P}(T,P)}{(-\epsilon P ln(\frac{P}{P^\circ}) + P\epsilon(T,P) - PT\frac{\partial \epsilon}{\partial T}(T,P))},$$

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

respectively.

Proof. The proof is the same as Lemma 31, using W instead of Z, noting that the error term $\epsilon(T,P)$ depends on P, unlike Lemma 51. □

Remark 7. We can formulate Lemmas 57 to 61 using Q instead of W, see Remark 6. 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 [6] as well.

11. 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 §10, we have following results;

Lemma 62 (The Nernst equation for the standard cell)**.** *At electrical chemical equilibrium (T,P) and (T,P°) for the standard cell, we have*

$$(E - E^\circ)(T,P) = -\frac{RTln(W(T,P))}{2F} - \frac{\epsilon(T,P)}{2F}.$$

Proof. Using the proof of Lemma 20, replacing $\epsilon(P)$ with the error term $\epsilon(T,P)$ from §10, noting that for the Gibbs function involving $c+1$ species, including the solvent, $(\frac{\partial G}{\partial \xi})_{T,P} = \sum_{i=1}^{c} \nu_i \mu_i$, we get the desired result. □

Lemma 63. *At electrical chemical equilibrium* (T,P) *and* (T,P°)*, and chemical equilibrium* (T,P)*, we have*

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

Proof. Following the proof of Lemma 21, replacing $\epsilon(P)$ with $\epsilon(T,P)$, we get our desired result. □

Lemma 64. *If* $\epsilon = 0$*, we have, for all* $T_1 > 0$*,*

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

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. The result can be obtained by following the proof of Lemma 22, replacing the result there that $(\frac{\partial G_{chem'}}{\partial \xi})_{T,P}$ is independent of P, with the corresponding result in Lemma 60. □

Lemma 65. *We have, for all* $T_1 > 0, P_1 > 0$*, that*

$$2F(E(T_1,P_1) - E^\circ(T_1)) = (\frac{\partial G}{\partial \xi})_{T,P}|_{(T_1,P_1)} - (\frac{\partial G}{\partial \xi})_{T,P}|_{(T_1,P_1^\circ)} - RT_1 ln(Z(T_1,P_1)) - \epsilon(T_1,P_1). \quad (120)$$

Proof. The result follows by following the proof of Lemma 23 and replacing $\epsilon(P)$ with $\epsilon(T,P)$. □

Remark 8. The result of Lemma 65 combined with the determination of the activity coefficient W in Lemma 60 and the error term $\epsilon(T,P)$ in Lemma 57 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 60 and then use the formula (120) in Lemma 65. Once this is determined, we then alter the power supply, in accordance with (120), to push the reaction along the paths of maximal reaction given in Lemma 61. 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.

12. The constant change in enthalpy assumption

Lemma 66. *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;

$$\begin{aligned}
\Delta H^{\circ,solv}(T) &= \Delta H^{\circ,solv}(T_0) + \int_{T_0}^{T} \frac{d(\Delta H^{\circ,solv}(T))}{dT} dT \\
&= \Delta H^{\circ,solv}(T_0) + \int_{T_0}^{T} \frac{d(\Delta Q_{solv}(T))}{dT} dT \\
&= \Delta H^{\circ,solv}(T_0) + \int_{T_0}^{T} C_{solv}(T) dT \\
&= \Delta H^\circ(T_0) + \int_{T_0}^{T} C_{solv}(T) dT, \quad (121)
\end{aligned}$$

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

$$\begin{aligned}
C_{solv}(T) &= C_{fin,solv}(T) - C_{in,solv}(T) \\
&= \frac{1}{m_{mix,solv}}\Big(\sum_{i=0}^{c} m_{i,fin}C_{i,fin}(T) - \sum_{i=1}^{c} m_{i,in}C_{i,in}(T)\Big) \\
&= \frac{N_A}{m_{mix,solv}}\Big(\sum_{i=0}^{c} n_{i,fin}m_{i,molec}C_{i,fin}(T) - \sum_{i=0}^{c} n_{i,in}m_{i,molec}C_{i,in}(T)\Big) \\
&= \frac{N_A}{m_{mix,solv}}\Big(\sum_{i=0}^{c} n_{i,fin}m_{i,molec}m_{i,fin}SC_i(T) - \sum_{i=0}^{c} n_{i,in}m_{i,molec}m_{i,in}SC_i(T)\Big) \\
&= \frac{N_A^2}{m_{mix,solv}}\Big(\sum_{i=0}^{c} n_{i,fin}^2 m_{i,molec}^2 SC_i(T) - \sum_{i=0}^{c} n_{i,in}^2 m_{i,molec}^2 SC_i(T)\Big) \\
&= \frac{N_A^2}{m_{mix,solv}}\Big(\sum_{i=0}^{c} (n_{i,in} - \nu_i)^2 m_{i,molec}^2 SC_i(T) - \sum_{i=0}^{c} n_{i,in}^2 m_{i,molec}^2 SC_i(T)\Big) \\
&= -\frac{2}{m_{mix,solv}}\Big(\sum_{i=1}^{c} \nu_i m_{i,in} m_{i,mol} SC_i(T)\Big) + \frac{1}{m_{mix,solv}}\Big(\sum_{i=1}^{c} \nu_i^2 m_{i,mol}^2 SC_i(T)\Big) \\
&= \theta(T) + v(T),
\end{aligned} \tag{122}$$

where $\nu_0 = 0$ and ν_i, for $1 \leq i \leq c$ are the stochiometric coefficients for the original reaction, (2).

Using the fact that $\frac{m_{i,in}}{m_{mix,solv}} \rightarrow 0$, for $1 \leq i \leq c$, by increasing the mass of the solvent not involved in the reaction, we have that $\theta(T) \rightarrow 0$, and, similarly, $v(T) \rightarrow 0$ as $m_{mix} \rightarrow \infty$ 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 $m_{mix,solv} \rightarrow \infty$, which we can achieve, by increasing the solvent not involved in the reaction, $C_{solv}(T) \rightarrow 0$. We then have, by $(M), (N)$, that

$$\Delta H^\circ(T) = \Delta H^\circ(T_0) + \int_{T_0}^{T} (\theta(S) + v(S))dS \rightarrow \Delta H^\circ(T_0),$$

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), for $1 \leq i \leq c$. □

13. Independence of path and existence

Lemma 67. *If $\lambda \neq 0$, see Lemma 7, then no substance is formed in a loop. With the assumption that ΔH^{circ} is constant, we have that $\lambda = \Delta H^\circ - \epsilon ln(P^\circ)$. 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 §12, for the mass of the mixture sufficiently large, we have that $\lambda(T_1, T_2) \simeq \Delta H^{\circ,ref}(T_1, T_2) - \epsilon(T_1, T_2) ln(P^\circ)$, where $\epsilon((T_1, T_2))$ can be effectively determined.*

Proof. Suppose that an amount of substance ξ is formed in a loop. We have, by Lemma 1, that

$$dG = -SdT + VdP + \sum_{i=1}^{c} \mu_i dn_i, \tag{123}$$

---

[2] During the paper, we denoted by substance 0 a solvent either involved or not involved in the reaction. Here, we are relabeling 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.

and, by the definition of enthalpy in Definition 1, that

$$dH = d(U + PV) = dU + PdV + VdP, \tag{124}$$

$$d(G + TS) = dG + TdS + SdT. \tag{125}$$

We then have that, for a closed path γ, using (123), (124), (125), the definition of entropy as $dS = \frac{dQ}{T}$ and the first law of thermodynamics, $dQ = dU + pdV$, the calculation of $(\frac{\partial G}{\partial \xi})_{(T,P)}$ as follows;

$$\begin{aligned}
\int_\gamma (dG + SdT - VdP) &= \int_\gamma ((dH - TdS - SdT) + SdT - VdP) \\
&= \int_\gamma (dH - TdS - VdP) \\
&= \int_\gamma (dH - dQ - VdP) \\
&= \int_\gamma ((dU + PdV + VdP) - dQ - VdP) \\
&= \int_\gamma (dU + PdV - dQ) \\
&= \int_\gamma ((dQ - PdV) + PdV - dQ) \\
&= 0,
\end{aligned}$$

$$\begin{aligned}
\int_\gamma (\sum_{i=1}^{c} \mu_i dn_i) &= \int_\gamma (\sum_{i=1}^{c} \mu_i \nu_i d\xi \\
&= \int_\gamma (\frac{\partial G}{\partial \xi})_{(T,P)} d\xi \\
&= \int_\gamma (\lambda + \epsilon ln(P) + \beta T + \sigma ln(T)) d\xi \\
&= \int_\gamma (\lambda + \epsilon ln(P) + \beta T + \sigma ln(T)) d\xi \\
&= \lambda \xi + \int_\gamma (\epsilon ln(P)\theta(P)dP + (\beta T + \sigma ln(T))\phi(T)dT),
\end{aligned} \tag{126}$$

where $\theta(P) = \theta_1(P)$ along γ_1, $\theta_1(P)dP = d\xi|_{\gamma_1}$, $\theta(P) = \theta_2(P)$ along γ_2, $\theta_2(P)dP = d\xi|_{\gamma_2}$, $\phi(T) = \phi_1(T)$ along γ_1, $\phi_1(T)dT = d\xi|_{\gamma_1}$, $\phi(T) = \phi_2(T)$ along γ_2, $\phi_2(T)dT = d\xi|_{\gamma_2}$.

Now, by Stokes Theorem;

$$\int_\gamma (\epsilon ln(P)\theta(P)dP + \beta T\phi(T)dT) = \int \int_R (\frac{\partial((\beta T + \sigma ln(T))\phi(T))}{\partial P} - \frac{\partial(\epsilon ln(P)\theta(P))}{\partial T}) dTdP = 0, \tag{127}$$

and, by (126), $\xi = 0$, if $\lambda \neq 0$. The second claim, with the assumption that ΔH° is constant, follows from the proof of Lemma 7, and in later sections, when we introduce error terms. The next claim follows easily as $w(T_1, T_2) \simeq 0$, see §12, 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 7. □

H1 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. Even if $\lambda = 0$, 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 $\Delta H = \int_\gamma dH = \int_\gamma d(U + VP) = \int_\gamma dU + PdV + VdP = \int_\gamma dU + dL + VdP = \Delta U + \Delta L + \int_\gamma VdP \simeq \Delta U + \Delta L + V_0 \int_\gamma dP = \Delta U + \Delta L = \Delta Q$.

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 $\Delta H = \int_\gamma VdP$, then, by generic considerations of bond energies, the amount of substance ξ formed by the reaction would also be quite small. If **H**1 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;

$$\begin{aligned} \xi &= \frac{n_i-n_{i,0}}{\nu_i}, & \\ n_i &= \nu_i\xi+n_{i,0}, & 1\leq i\leq c), \end{aligned}$$

we must have that

$$x_i=\frac{n_i}{n}=\frac{\nu_i\xi+n_{i,0}}{\sum_{i=1}^{c}(\nu_i\xi+n_{i,0})}=\frac{\nu_i\xi+n_{i,0}}{\lambda\xi+n_0}=f_i, \qquad 1\leq i\leq c,$$

where $\lambda=\sum_{i=1}^{c}\nu_i$, so that

$$\begin{aligned} \nu_i\xi+n_{i,0} &= (\lambda\xi+n_0)f_i, & \\ \xi &= \frac{n_{i,0}-n_0f_i}{\kappa f_i-\nu_i}, & 1\leq i\leq c, \end{aligned}$$

so that, for $1\leq i\leq j\leq c$, we have

$$\frac{n_{i,0}-n_0f_i}{\kappa f_i-\nu_i}=\frac{n_{j,0}-n_0f_j}{\kappa f_j-\nu_i}=\xi. \tag{128}$$

As all the steps are reversible, the requirement (128) at (T,P), for all $(n_{1,0},\dots,n_{c,0})$ satisfying $\frac{n_{i,0}}{n_0}=f_i(T_0,P_0)$, so that

$$\xi(T_0,P_0)=0 \tag{129}$$

is equivalent to **H**1. We impose the condition that $Ker(M)\cap\mathcal{R}^c_{>0}\neq\emptyset$, where

$$\begin{aligned} M_{ii} &= f_i(T_0,P_0)-1, & 1\leq i\leq c, \\ M_{ij} &= f_i(T_0,P_0), & 1\leq i<j\leq c, \end{aligned}$$

so that there exists at least one choice $(n_{1,0},\dots,n_{c,0})\in\mathcal{R}^c_{>0}$ satisfying (129). With this requirement there do exist feasible paths between any 2 pairs (A,B), see Lemma 12. If not, there is no feasible path involving a reaction from $A=(T_0,P_0)$, which seems physically unreasonable.

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.

Conflicts of Interest: "The author declares no conflict of interest."

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