Supporting Information

Stability of Liquid Water Phase on Mars: A Thermodynamic Analysis Considering Martian Atmospheric Conditions and Perchlorate Brine Solutions

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Supplementary Material S1

Solubility Data

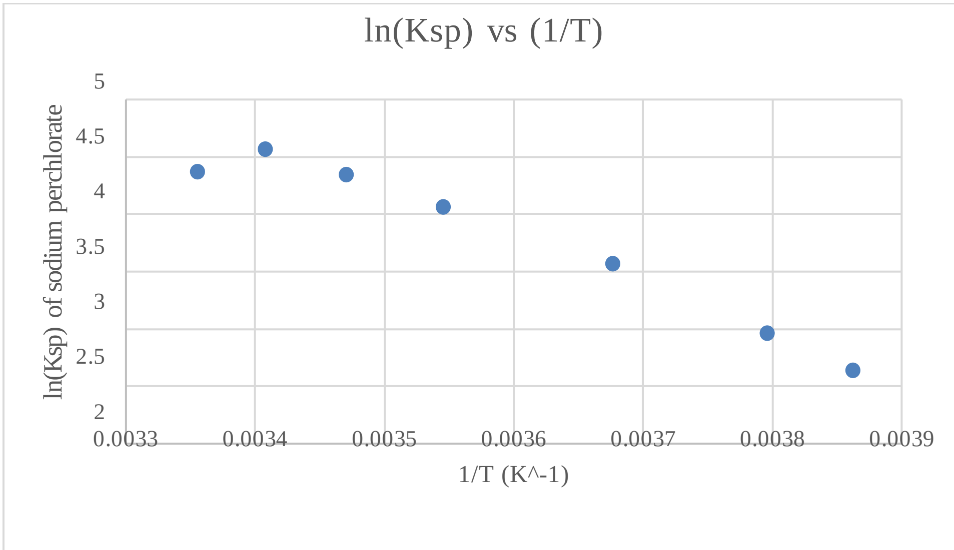

Figure S1. Solubility data of sodium perchlorate

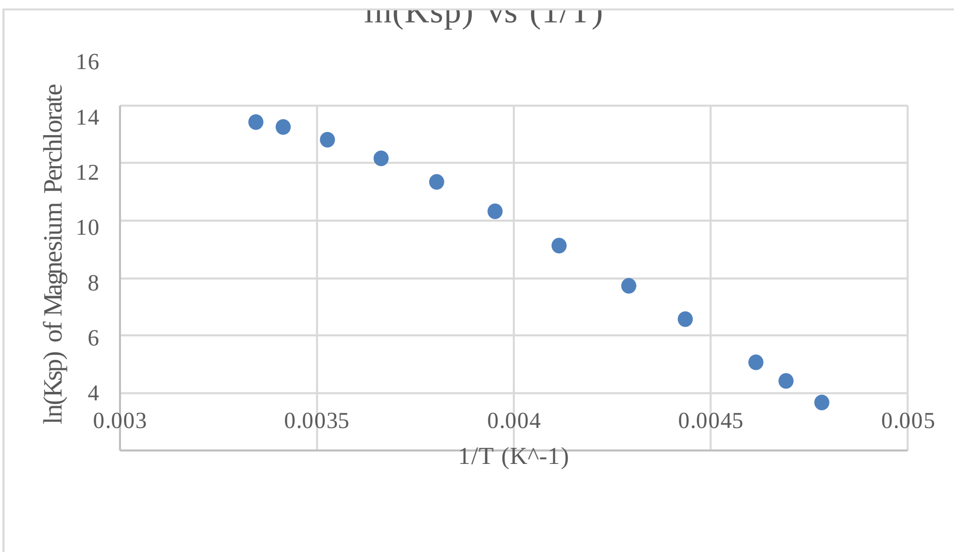

Figure S2. Solubility data of magnesium perchlorate

Supplementary Material S2

Computer Code used for solving Pitzer equations

A simplified form of Pitzer equation (excluding neutral species) is as given as:

$$\phi = 1 + \frac{2}{\sum m_i}\left\{ \frac{-A_\phi I^{\frac{3}{2}}}{1 + bI^{\frac{1}{2}}} + \sum\sum m_c m_a \left(\beta^{\phi}_{ca} + ZC_{ca}\right) + \sum\sum m_c m_{c'} \left(\Phi^{\phi}_{cc'} + \sum m_a \psi_{cc'a}\right) + \sum\sum m_a m_{a'} \left(\Phi^{\phi}_{aa'} + \sum m_c \psi_{ca'a}\right) \right\} \qquad \text{(i)}$$

$$\ln \gamma_M = z_M^2 F + \sum m_a \left(2\beta_{Ma} + ZC_{Ma}\right) + \sum m_c \left(2\Phi_{Mc} + \sum m_a \psi_{Mca}\right) + \sum\sum m_a m_{a'} \psi_{Maa'} + |z_M| \sum\sum m_c m_a C_{ca} \qquad \text{(ii)}$$

$$\ln \gamma_X = z_X^2 F + \sum m_c \left(2\beta_{cX} + ZC_{cX}\right) + \sum m_a \left(2\Phi_{Xa} + \sum m_c \psi_{cXa}\right) + \sum\sum m_c m_{c'} \psi_{cc'X} + |z_X| \sum\sum m_c m_a C_{ca} \qquad \text{(iii)}$$

Where, z_i denotes the charge of the corresponding ion,

'c' denotes cat-ion, 'a' denotes anion,

m_i denotes molality of the corresponding ion,

I is the ionic strength, I = $\frac{1}{2} \times \sum m_i z^2{}_i$

A_ϕ is the Debye Huckel limiting law slope, A_ϕ = 0.3917 $m^{-0.5}$ at 298 K,

b is a constant, b = 1.2 $m^{-0.5}$,

Z = $\sum m_i z_i$

$$\beta^{\phi}{}_{MX} = \beta^{(0)}{}_{MX} + \beta^{(1)}{}_{MX} \exp(-\alpha_1 \sqrt{I}) \qquad \text{(iv)}$$

$$\beta_{MX} = \beta^{(0)}{}_{MX} + \beta^{(1)}{}_{MX}\, g(-\alpha_1 \sqrt{I}) \qquad \text{(v)}$$

$$C_{MX} = \frac{C^{\phi}{}_{MX}}{2\sqrt{|z_M z_X|}} \qquad \text{(vi)}$$

$$\Phi_{ij}^{\phi} = \theta_{ij} + {}^{E}\theta_{ij} + I\frac{d\,{}^{E}\theta_{ij}}{dI} \quad \text{(vii)}$$

$$\Phi_{ij} = \theta_{ij} + {}^{E}\theta_{ij} \quad \text{(viii)}$$

$$F = -A_{\phi}\left[\frac{\sqrt{I}}{1+b\sqrt{I}} + \frac{2}{b}\ln(1+b\sqrt{I})\right] + \sum\sum m_c m_a \beta'_{ca} + \sum\sum m_c m_{c'} \Phi'_{cc'} + \sum\sum m_a m_{a'} \Phi'_{aa'} \quad \text{(ix)}$$

$$g(x) = \frac{2}{x^2}\left[1-(1+x)\exp(-x)\right] \quad \text{(x)}$$

Activity of water, $a_w = \exp\left(\frac{-\phi\sum m_i}{55.5084}\right)$ (xi)

ϕ is the osmotic coefficient of water

The parameters $\beta^{\phi}{}_{MX}$, β_{MX}, $C^{\phi}{}_{MX}$, ψ are dependent on temperature and temperature dependence is given by the equation [16],

P = A + B(T-298.15) + C(T-298.15)^2 (xii)

Where, P can be any of the above parameters.

The standard values of $\beta^{\phi}{}_{MX}$, β_{MX}, $C^{\phi}{}_{MX}$ are taken from FREZCHEM [10] and the values of parameters A, B, C for each of the above are given in the table below. The method of determination of parameters B and C has been explained in detail in the work of Toner et.al [21]. Only the values given in table 3 in that work were taken as such, whereas $\psi_{Na^+,Mg^{2+},ClO^-{}_4}$ and $\theta_{Na^+,Mg^{2+}}$ were determined independently in this work as explained later.

Table S1. Pitzer parameter values [21]

Parameter	A	B	C
$\beta^{(0)}{}_{Na^+,ClO^-{}_4}$	5.54E-2	7.8712E-4	-3.8727E-6
$\beta^{(1)}{}_{Na^+,ClO^-{}_4}$	2.755E-1	4.4318E-3	-1.2331E-4
$C^{\phi}{}_{Na^+,ClO^-{}_4}$	-1.18E-3	-5.3394E-5	3.9507E-7
$\beta^{(0)}{}_{Mg^{2+},ClO^-{}_4}$	4.9613E-1	4.9397E-4	-2.7085E-6
$\beta^{(1)}{}_{Mg^{2+},ClO^-{}_4}$	2.0085E0	5.0772E-3	-4.2302E-4
$C^{\phi}{}_{Mg^{2+},ClO^-{}_4}$	9.581E-3	-3.4602E-4	-2.1062E-7

The values of $\psi_{Na^+,Mg^{2+},ClO^-{}_4}$ and $\theta_{Na^+,Mg^{2+}}$ are 0 for binary solutions.

Table S2. Data of calculated osmotic coefficient against experimental osmotic coefficient [8]

Temperature, K	Molality of sodium perchlorate, m1	Molality of magnesium perchlorate, m2	m1+m2	Osmotic coefficient, phi, experimental [21]	Osmotic coefficient, phi, calculated
268.89	**0.354**	**0.636**	**0.99**	**0.9744**	**0.974**
266.86	**0.494**	**0.889**	**1.383**	**1.0317**	**1.033**
262.78	**0.740**	**1.331**	**2.071**	**1.1437**	**1.144**
258.94	**0.935**	**1.682**	**2.617**	**1.240**	**1.24**
254.66	**1.134**	**2.040**	**3.174**	**1.000**	**1.343**
250.36	**1.298**	**2.334**	**3.632**	**1.4342**	**1.434**
242.56	**1.571**	**2.826**	**4.397**	**1.5953**	**1.596**
238.56	**1.678**	**3.019**	**4.697**	**1.6627**	**1.663**

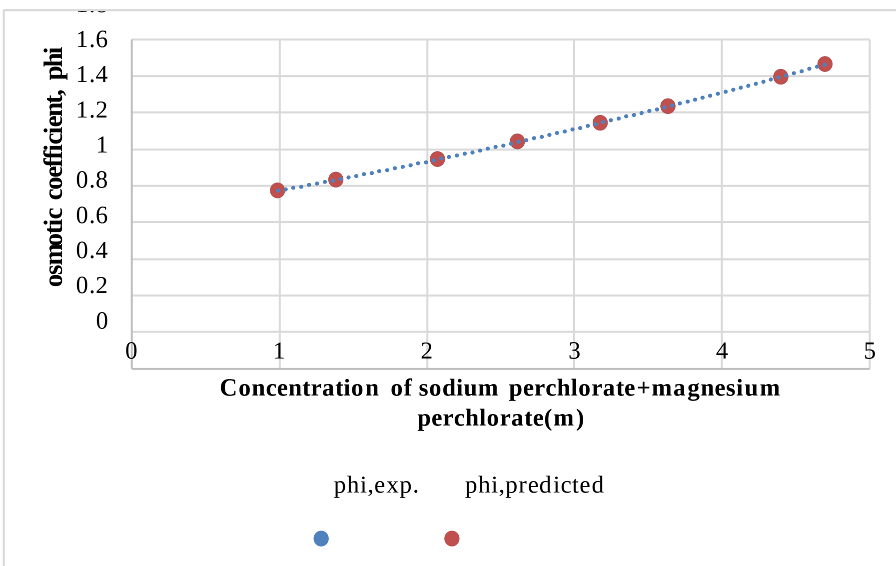

Figure S3. Plot of osmotic pressure, experimental and predicted used for computation of $\psi_{Na^+,Mg^{2+},ClO^-_4}$ and $\theta_{Na^+,Mg^{2+}}$

Code 1: For calculating Eutectic freezing point temperatures of Sodium Perchlorate

```
function f = v2(x)

f = zeros(2,1);

z = [1,-1];

A = [5.54E-2;2.755E-1;-1.18E-3];

B = [7.8712E-4;4.4318E-3;-5.3394E-5];

C = [-3.8727E-6;-1.2331E-4;3.9507E-7];

Aphi = 0.3917;

b = 1.2;

m = x(1);

T = x(2);

Td = T;

    M = 2*m;

    I =  0.5*(m*z(1)^2+m*z(2)^2);

    y = (2*(I^0.5));

    g = (2*(1-((1+y)*exp(-y)))/y^2);

dg =  (2*(1-((1+y+(0.5*y^2))*exp(-y)))/y^2);

    beta0Na = (A(1)+ B(1)*(T-298.15)+ (C(1)*(T- 298.15)^2));

    beta1Na = (A(2) + B(2)*(T-298.15)+ (C(2)*(T- 298.15)^2));

CphiNa = (A(3) + B(3)*(T-298.15)+ (C(3)*(T- 298.15)^2));

BphiNa  =(beta0Na + ((beta1Na)*exp(-y)));

BNa = (beta0Na + (beta1Na*g));

BdNa = (beta1Na*dg/I);

    Z =(m*z(1) - m*z(2)) ;

CNa=  (CphiNa/2);

    F = (-Aphi*(((I^0.5)/(1+(b*I^0.5))) + (2/1.2)*log(1+(b*(I^0.5)))) + (m*m*BdNa)) ;

lngammaNa = (F + m*(2*BNa + Z*CNa) + m*m*CNa);
```

```
lngammaCl = (F + m*(2*BNa + Z*CNa) + m*m*CNa);

phi = ( 1 + (2/M)*(((-Aphi*(I^1.5))/(1+(b*I^0.5))) + m*m*(BphiNa + (Z*CNa)))) ;


gammaNa = exp(lngammaNa)

gammaCl = exp(lngammaCl)

    aw2 = exp((-phi*M)/55.50844)


    Kcal = (gammaNa*gammaCl*(m^2)*aw2^2);

Kc = log(Kcal);

    K = (-5E-4*Td^2) + (0.3288*Td) - 49.3636;

    T

    Td

f(1)= Td - 273.15 + ((6004.8 - (4541.94*log(aw2)) - ((47119143.38*log(aw2)) + 36057623.04)^0.5)/(81.947 - 16.628*log(aw2)));

f(2)  = K-Kc;

end
```

Code 2 : For calculating Eutectic freezing point temperature of Magnesium Perchlorate

```
function f = v5(x)

f = zeros(2,1);

z = [2,-1];

A = [4.9613E-1;2.0085E0;9.581E-3];

B = [4.9397E-4;5.0772E-3;-3.4602E-4];

C = [-2.7085E-6;-4.2302E-4;-2.1062E-7];

Aphi = 0.3917;

b = 1.2;

m = x(1);

T = x(2);
```

```
Td = T;
        M = 3*m;
        I =  0.5*(m*z(1)^2+(2*m*z(2)^2));
        y = (2*(I^0.5));
        g = (2*(1-((1+y)*exp(-y)))/y^2);
dg =  (2*(1-((1+y+(0.5*y^2))*exp(-y)))/y^2)
        beta0Mg = (A(1)+ B(1)*(T-298.15)+ (C(1)*(T- 298.15)^2));
        beta1Mg = (A(2) + B(2)*(T-298.15)+ (C(2)*(T- 298.15)^2));
CphiMg = (A(3) + B(3)*(T-298.15)+ (C(3)*(T- 298.15)^2));
BphiMg  =(beta0Mg + ((beta1Mg)*exp(-y)));
BMg = (beta0Mg + (beta1Mg*g));
BdMg = (beta1Mg*dg/I);
        Z =(m*z(1) - m*z(2)) ;
CMg=  (CphiMg/(2^1.5));
        F = (-Aphi*(((I^0.5)/(1+(b*I^0.5))) + (2/1.2)*log(1+(b*(I^0.5)))) + (2*m*m*BdMg)) ;
lngammaMg = (4*F + 2*m*(2*BMg + Z*CMg) + 4*m*m*CMg);
lngammaCl = (F + m*(2*BMg + Z*CMg) + 2*m*m*CMg);
phi = ( 1 + (2/M)*(((-Aphi*(I^1.5))/(1+(b*I^0.5))) + 2*m*m*(BphiMg + (Z*CMg)))) ;


gammaMg = exp(lngammaMg)
gammaCl = exp(lngammaCl)
        aw2 = exp((-phi*M)/55.50844)
gamma = (gammaMg*(gammaCl^2));


        Kcal = (gamma*m*((2*m)^2)*(aw2^6));
Kc = log(Kcal);
        K = (-0.0009*T^2) + (0.5881*T) - 76.0746;
```

```
    T

      Td

f(1)= Td - 273.15 + ((6004.8 - (4541.94*log(aw2)) - ((47119143.38*log(aw2)) + 36057623.04)^0.5)/(81.947 -
16.628*log(aw2)));

f(2)  = K - Kc;

end
```

Code 3 : For calculating Eutectic freezing point temperature of Sodium Perchlorate-Magnesium Perchlorate-Water solution

```
function f = v14(x)

%FP of Ternary Mixture

f = zeros(2,1);

z = [1,2,-1];

A = [5.54E-2;2.755E-1;-1.18E-3;4.9613E-1;2.0085;9.581E-3;-0.0274];

B = [7.8712E-4;4.4318E-3;-5.3394E-5;4.9397E-4;5.0772E-3;-3.4602E-4];

C = [-3.8727E-6;-1.2331E-4;3.9507E-7;-2.7085E-6;-4.2302E-4;-2.1062E-7];

theta = -0.0043;

Aphi = 0.3917;

b = 1.2;


m1 = 3;

m2 = 3;

m3 = m1 + 2*m2;

T = x(1);

Td = T;


  p = 0.0107*(m1+m2)^2 + 0.1248*(m1+m2) + 0.8396;

  M = 2*m1 + 3*m2;
```

S10

```
I = 0.5*(m1*z(1)^2+ m2*z(2)^2+m3*z(3)^2);

y = 2*I^0.5;

g = 2*(1-((1+y)*exp(-y)))/y^2;

dg = 2*(1-((1+y+(0.5*y^2))*exp(-y)))/y^2;

beta0Na = A(1) + B(1)*(T-298.15)+ (C(1)*(T- 298.15)^2);

beta0Mg = A(4) + B(4)*(T-298.15)+ (C(4)*(T- 298.15)^2);

beta1Na = A(2) + B(2)*(T-298.15)+ (C(2)*(T- 298.15)^2);

beta2Mg = A(5) + B(5)*(T-298.15)+ (C(5)*(T- 298.15)^2);

CphiNa = A(3) + B(3)*(T-298.15)+ (C(3)*(T- 298.15)^2);

CphiMg = A(6) + B(6)*(T-298.15)+ (C(6)*(T- 298.15)^2);

Si = A(7) ;

BphiNa = beta0Na + (beta1Na*exp(-y));

BNa = beta0Na + (beta1Na*g);

BdNa = beta1Na*dg/I;

BphiMg = beta0Mg + (beta2Mg*exp(-y));

BMg = beta0Mg + (beta2Mg*g);

BdMg = beta2Mg*dg/I;

m1

m2

Z = m1*z(1) + m2*z(2) - m3*z(3)

CNa = CphiNa/2;

CMg = CphiMg/(2^1.5);

F = -Aphi*(((I^0.5)/(1+(b*I^0.5))) + (2/1.2)*log(1+(b*(I^0.5)))) + (m1*m3*BdNa) + (m2*m3*BdMg) +
(m1*m2*theta);

lngammaNa = F + m3*(2*BNa + Z*CNa) + m2*(2*theta + m3*Si) + m1*m3*CNa + m2*m3*CMg;

lngammaMg = (z(2)^2)*F + m3*(2*BMg + Z*CMg) + m1*(2*theta + m3*Si) + z(2)*(m2*m3*CMg +
m1*m3*CNa);

lngammaCl = F + m1*(2*BNa + Z*CNa) + m2*(2*BMg + Z*CMg) + m1*m2*Si + m1*m3*CNa + m2*m3*CMg;
```

```
phi  = 1 + (2/M)*(((-Aphi*(I^1.5))/(1+(b*I^0.5))) + m2*m3*(BphiMg + (Z*CMg)) + m1*m3*(BphiNa + (Z*CNa)) + m1*m2*(theta + m3*Si));

gammaNa = exp(lngammaNa)

gammaMg = exp(lngammaMg)

gammaCl = exp(lngammaCl)

   aw2 = exp((-phi*M)/55.50844)

KcalNa = (gammaNa*gammaCl*m1^2*aw2^2);

KcNa = log(KcalNa);

KNa = (-0.0003*T^2) + (0.1747*T) - 24.4908;

KcalMg = (gammaMg*(gammaCl^2)*m2*(2*m2)^2*aw2^6);

KcMg = log(KcalMg);

KMg = (-0.0011*T^2) - (0.4766*T) + 55.4051;

f(1) = Td - 273.15 + ((6004.8 - (4541.94*log(aw2)) - ((47119143.38*log(aw2)) + 36057623.04)^(1/2))/(81.947 - 16.628*log(aw2)));
```

Similar codes were used for finding out the highest boiling temperature of the solutions by using equation xxi given in the paper.

Code 4: For computing $\psi_{Na^+,Mg^{2+},ClO^-_4}$ **and** $\theta_{Na^+,Mg^{2+}}$

```
function f = theta1(x)

f = zeros(2,1);

z = [1,2,-1];

A = [5.54E-2;2.755E-1;-1.18E-3;4.9613E-1;2.0085;9.581E-3];

B = [7.8712E-4;4.4318E-3;-5.3394E-5;4.9397E-4;5.0772E-3;-3.4602E-4];

C = [-3.8727E-6;-1.2331E-4;3.9507E-7;-2.7085E-6;-4.2302E-4;-2.1062E-7];

theta = x(2);

Aphi = 0.3917;

b = 1.2;

m1 = 7.87;
```

```
m2 = 3.11;

m3 = m1 + 2*m2;

T = 298.15;

Td = T;


    M = 2*m1 + 3*m2;

    I = 0.5*(m1*z(1)^2+ m2*z(2)^2+m3*z(3)^2);

    y = 2*I^0.5;

    g = 2*(1-((1+y)*exp(-y)))/y^2;

    dg = 2*(1-((1+y+(0.5*y^2))*exp(-y)))/y^2;

    beta0Na = A(1) + B(1)*(T-298.15)+ (C(1)*(T- 298.15)^2);

    beta0Mg = A(4) + B(4)*(T-298.15)+ (C(4)*(T- 298.15)^2);

    beta1Na = A(2) + B(2)*(T-298.15)+ (C(2)*(T- 298.15)^2);

    beta2Mg = A(5) + B(5)*(T-298.15)+ (C(5)*(T- 298.15)^2);

    CphiNa = A(3) + B(3)*(T-298.15)+ (C(3)*(T- 298.15)^2);

    CphiMg = A(6) + B(6)*(T-298.15)+ (C(6)*(T- 298.15)^2);

    Si = x(1);

    BphiNa = beta0Na + (beta1Na*exp(-y));

    BNa = beta0Na + (beta1Na*g);

    BdNa = beta1Na*dg/I;

    BphiMg = beta0Mg + (beta2Mg*exp(-y));

    BMg = beta0Mg + (beta2Mg*g);

    BdMg = beta2Mg*dg/I;

    Z = m1*z(1) + m2*z(2) - m3*z(3)

    CNa = CphiNa/2;

    CMg = CphiMg/(2^1.5);
```

```
    F = -Aphi*(((I^0.5)/(1+(b*I^0.5))) + (2/1.2)*log(1+(b*(I^0.5)))) + (m1*m3*BdNa) + (m2*m3*BdMg) +
(m1*m2*theta);

    lngammaNa = F + m3*(2*BNa + Z*CNa) + m2*(2*theta + m3*Si) + m1*m3*CNa + m2*m3*CMg;

    lngammaMg = (z(2)^2)*F + m3*(2*BMg + Z*CMg) + m1*(2*theta + m3*Si) + z(2)*(m2*m3*CMg +
m1*m3*CNa);

    lngammaCl = F + m1*(2*BNa + Z*CNa) + m2*(2*BMg + Z*CMg) + m1*m2*Si + m1*m3*CNa +
m2*m3*CMg;

    phi  = 1 + (2/M)*(((-Aphi*(I^1.5))/(1+(b*I^0.5))) + m2*m3*(BphiMg + (Z*CMg)) + m1*m3*(BphiNa +
(Z*CNa)) + m1*m2*(theta + m3*Si));

    gammaNa = exp(lngammaNa)

    gammaMg = exp(lngammaMg)

    gammaCl = exp(lngammaCl)

    aw2 = exp((-phi*M)/55.50844)

    y = 1E-3*m1^3 - 3.37E-2*m1^2 + 6.09E-2*m1 + 4.353;


        KcalNa = (gammaNa*gammaCl*m1^2*aw2);

        KcNa = log(KcalNa);

        KNa = (-0.0005*Td^2) + (0.3318*Td) - 50.116;

        KcalMg = (gammaMg*(gammaCl^2)*m2*(2*m2)^3*aw2^6);

        KcMg = log(KcalMg);

        KMg = (-0.0009*Td^2) + (0.5881*Td) - 76.0746;

        f(1) = KNa -KcNa

        f(2) = KMg - KcMg

        theta

        Si

        m1

        m2


end
```