Appendix–A: Regression Modeling of Experimental Data

I) The Generalized Random Variable Linear Regression Model:

The model equation can be written as:

$$\hat{Y}_i = \beta_0 + \beta_1 x_i + \hat{\varepsilon}_i \qquad \text{-------------------- } (A_1)$$

Where:

$$\hat{\varepsilon}_i \equiv N\left[0, \sigma^2\right]$$

I-1) Confidence bound on $\hat{\beta}_0$ (100(1- α) % interval) is $\hat{\beta}_0 - \theta < \beta_0 \leq \hat{\beta}_0 + \theta$ **with** $\theta \equiv \left(t_{\alpha/2,(n-2)}\right) S_e\left(\hat{\beta}_0\right)$**.**

With the standard error of the intercept as:

$$S_e\left(\hat{\beta}_0\right) = \sqrt{MS_{res}\left(\frac{1}{n} + \frac{\overline{X}^2}{S_{XX}}\right)} \qquad \text{-------------------- } (A_2)$$

Where:

$$S_{XX} = \sum_{i=1}^{n}\left(x_i - \overline{X}\right)^2$$

$$MS_{res} = \text{ Residual Mean Square } = \frac{SS_{res}}{n-2} \equiv \hat{\sigma}^2$$

$$SS_{res} = SS_{Total} - \hat{\beta}_1 S_{XY}$$

$$\hat{\beta}_1 = \frac{S_{XY}}{S_{XX}} = \frac{\sum_{i-1}^{n} Y_i \left(X_i - \overline{X}\right)}{\sum_{i=1}^{n} \left(X_i - \overline{X}\right)^2} \qquad \text{-------------------- } (A_3)$$

$$SS_{Total} = \sum_{i=1}^{n} \left(Y_i - \overline{Y}\right)^2 \qquad \text{-------------------- } (A_4)$$

$$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n} \text{ and } \overline{Y} = \frac{\sum_{i=1}^{n} Y_i}{n} \qquad \text{-------------------- } (A_5)$$

$$\hat{\beta}_0 = \overline{Y} - \hat{\beta}_1 \overline{X}$$

n = Number of observations

$\left(t_{\alpha/2,(n-2)}\right)$ = "t" statistic

I-2) Confidence bound on $\hat{\beta}_1$ (100(1- α) % Estimate) is $\hat{\beta}_1 - \theta_1 < \beta_1 \le \hat{\beta}_1 + \theta_1$

With $\theta_1 \equiv \left(t_{\alpha/2,(n-2)}\right) S_e\left(\hat{\beta}_1\right)$

Where the standard error of the intercept is:

$$S_e\left(\hat{\beta}_1\right) = \sqrt{\frac{MS_{res}}{SS_{XX}}} \qquad \text{-------------------- } (A_6)$$

I-3) Interval Estimate of Expectation Value:

The estimate of the expectation value of $Y_i \left(\hat{\mu}_{Y_i/X_i} \right)$ can be written as:

$$\hat{E}\left(Y_i / X_i \right) = \hat{\mu}_{Y_i/X_i} = \hat{\beta}_0 + \hat{\beta}_1 X_i \qquad \text{-------------------- } (A_7)$$

The interval bounds for this parameter are:

$$\left[\hat{\mu}_{Y_i/X_i} - \theta_2 \right] < E\left(Y_i / X_i \right) \leq \left[\hat{\mu}_{Y_i/X_i} + \theta_2 \right] \qquad \text{-------------------- } (A_8)$$

With $\theta_2 \equiv \left(t_{\alpha/2,(n-2)} \right) \sqrt{MS_{res} \left[\frac{1}{n} + \frac{\left(X_i - \overline{X} \right)^2}{S_{XX}} \right]}$

I-4) New 'Prediction' Value:

The expressions are:

$$\left[\hat{Y}_i - \theta_3 \right] < Y_i \leq \left[\hat{Y}_i + \theta_3 \right] \qquad \text{-------------------- } (A_9)$$

With $\theta_3 \equiv \left(t_{\alpha/2,(n-2)} \right) \sqrt{MS_{res} \left[1 + \frac{1}{n} + \frac{\left(X_i - \overline{X} \right)^2}{S_{XX}} \right]}$

I-5) Coefficient of determination for generalized regression equation is:

$$R^2 = 1 - \frac{SS_{res}}{SS_{Total}} \qquad \text{-------------------- } (A_{10})$$

II) Constrained Random Variable Linear Regression Model:

The model equation can be written as:

$$\hat{Y}_i = \beta_2 x_i + \hat{\varepsilon}_i \qquad \text{-------------------- } (A_{11})$$

Where:

$$\hat{\varepsilon}_i \equiv N\left[0, \sigma^2\right] \text{ with } \hat{\sigma}^2 = MS_{res} \equiv \frac{\sum_{i=1}^{n}\left(Y_i - \hat{Y}_i\right)^2}{n-1}$$

$$\hat{\beta}_2 = \frac{\sum_{i-1}^{n} X_i Y_i}{\sum_{i=1}^{n} X_i^2} \qquad \text{-------------------- } (A_{12})$$

II-1) Confidence bound on $\hat{\beta}_2$ (100(1- α) % interval) is $\hat{\beta}_2 - \theta_4 < \beta_2 \le \hat{\beta}_2 + \theta_4$ with $\theta_4 \equiv \left(t_{\alpha/2,(n-2)}\right) S_e\left(\hat{\beta}_2\right)$.

Where the standard error of the intercept is:

$$S_e\left(\hat{\beta}_2\right) = \sqrt{\frac{MS_{res}}{\sum_{i=1}^{n} X_i^2}} \qquad \text{-------------------- } (A_{13})$$

II-2) Interval Estimate of Expectation Value:

The estimate of the expectation value of $Y_i\left(\hat{\mu}_{Y_i/X_i}\right)$ can be written as:

$$\hat{E}\left(Y_i/X_i\right) = \hat{\mu}_{Y_i/X_i} = \hat{\beta}_2 X_i \qquad \text{-------------------- } (A_{14})$$

The interval bounds for this parameter are

$$\left[\hat{\mu}_{Y_i/X_i} - \theta_5\right] < E\left(Y_i/X_i\right) \leq \left[\hat{\mu}_{Y_i/X_i} + \theta_5\right] \qquad \text{-------------------- } (A_{15})$$

With $\theta_5 \equiv \left(t_{\alpha/2,(n-1)}\right)\sqrt{\dfrac{X_i^2\left(MS_{res}\right)}{\sum_{i=1}^{n} X_i^2}}$

II-3) New "Prediction" Value:

The expressions are:

$$\left[\hat{Y}_i - \theta_6\right] < Y_i \leq \left[\hat{Y}_i + \theta_6\right] \qquad \text{-------------------- } (A_{16})$$

With $\theta_6 \equiv \left(t_{\alpha/2,(n-1)}\right)\sqrt{MS_{res}\left[1 + \dfrac{X_i^2}{\sum_{i}^{n} X_i^2}\right]}$

II-4) Coefficient of determination for constrained regression equation is:

$$R_0^{\ 2} = \frac{\sum_{i=1}^{n} \hat{Y}_i^2}{\sum_{i=1}^{n} Y_i^2} \qquad \text{-------------------- } (A_{17})$$

Appendix–B: Formulations of Van't Hoff Relation

Two different derivations of the form of the "Van't Hoff" expression are presented as below:

Derivation–1:

The Clausius – Clapeyron equation is given by:

$$\frac{d(\ln P)}{dT} = \frac{\Delta H^{l \to v}}{RT^2} \qquad \text{--------------------- (B}_1\text{)}$$

The above equation describes a vapor – condensed phase equilibrium of the form:

$$\alpha_{liquid} \Leftrightarrow \alpha_{vapor} \qquad \text{--------------------- (B}_2\text{)}$$

On the other hand (in our case), the reaction is considering of the form:

$$\alpha_{solid} + H_{2(gas)} \Leftrightarrow \alpha H_{2(solid)} \qquad \text{--------------------- (B}_3\text{)}$$

Assuming α_{solid} and αH_2 to be in standard state (pure substance),

$$\Delta G_T = \Delta G_T^0 + RT \ln K = \Delta G_T^0 + RT \ln \frac{a_{\alpha H_2}}{a_\alpha a_{H_2}} \qquad \text{--------------------- (B}_4\text{)}$$

Since, $a_{\alpha h_2} = a_\alpha = 1$, and $a_{H_2} = \dfrac{P_{h_2}}{P_{H_2}^0}$.

Therefore, Eqn. (B4) can write;

$$\therefore \Delta G_T = \Delta G_T^0 + RT \ln\left(\frac{1}{\frac{P_{H_2}}{P_{H_2}^0}}\right) \qquad \text{--------------------- } (B_5)$$

Now, at equilibrium at any temperature, $\Delta G_T \equiv 0$. This implies:

$$-\ln\left(\frac{P_{H_2}}{P_{H_2}^0}\right) = -\frac{\Delta G_T^0}{RT} \qquad \text{--------------------- } (B_6)$$

But, $\Delta G_T^0 = \Delta \mathrm{H}_T^0 - T\Delta S_T^0$

$$\therefore \ \ln\left(\frac{P_{H_2}}{P_{H_2}^0}\right) = \frac{\Delta H_T^0}{RT} - \frac{\Delta S_T^0}{R} \qquad \text{--------------------- } (B_7)$$

If $\Delta H_T^0 \neq \phi(T)$ and $\Delta S_T^0 \neq \phi(T)$, then Eqn. ($B_7$) can write:

$$\ln\left(\frac{P_{H_2}}{P_{H_2}^0}\right) = \left(\frac{\Delta H^0}{R}\right)\frac{1}{T} - \frac{\Delta S^0}{R} \qquad \text{--------------------- } (B_8)$$

$$\ln\left(\frac{P_{H_2}}{P_{H_2}^0}\right) = \frac{\alpha_1}{T} + \alpha_2 \qquad \text{--------------------- } (B_9)$$

With, $\alpha_1 = \frac{\Delta H^0}{R}$ and $\alpha_2 = -\frac{\Delta S^0}{R}$

If one now applies Eqns. (B_7) or (B_8) to two temperatures T_1 and T_2, we can write,

$$\ln\left(\frac{\left(P_{H_2}\right)_{T_2}}{P^0_{H_2}}\right)-\ln\left(\frac{\left(P_{H_2}\right)_{T_2}}{p^0_{H_2}}\right)=\frac{\Delta H^0}{R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right] \qquad \text{--------------------- (B}_{10}\text{)}$$

$$\ln\left(\frac{\left(P_{H_2}\right)_{T_2}}{\left(P_{H_1}\right)_{T1}}\right)=\frac{\Delta H^0}{R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right] \qquad \text{--------------------- (B}_{11}\text{)}$$

At this point, it is to be noted that in the chemical equilibrium considered for Eq. (B_7) or (B_8), the vapor (gaseous) phase is placed on the left hand side of Eq. (B_3). If in the condensation reaction considered by Eq. (B_2), the vapor phase is placed on the left hand side as:

$$\alpha_{vapor} \Leftrightarrow \alpha_{liquid} \qquad \text{--------------------- (B}_{12}\text{)}$$

Then, Clausius – Clapeyron equation will read:

$$\left(\frac{dP}{dT}\right)_{eq}=\frac{\Delta H^{v\to l}}{T\left(V^l-V^v\right)}\cong-\frac{\Delta H^{v\to l}}{TV^v} \qquad \text{--------------------- (B}_{13}\text{)}$$

$$\text{or } \left(\frac{dP}{P}\right)_{eq}=-\frac{\Delta H^{v\to l}}{RT^2} \qquad \text{--------------------- (B}_{14}\text{)}$$

On integration of above equation one obtains:

$$\ln P=\frac{\Delta H^{v\to l}}{RT}+\alpha_2 \qquad \text{--------------------- (B}_{15}\text{)}$$

$$\text{or } \quad \ln P=\frac{\alpha_1}{T}+\alpha_2 \qquad \text{--------------------- (B}_{16}\text{)}$$

or between station temperatures T_1 and T_2, we can write:

$$\ln \frac{P_2}{P_1} = \frac{\Delta H^{v \to l}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$ --------------------- (B_{17})

 # Derivation–2:

The Van't Hoff relationship can also deduce using the following two identities,

$$\left[\frac{\partial\left(\frac{\Delta G^0}{T}\right)}{\partial T}\right]_P = -\frac{\Delta H^0}{T^2}$$ --------------------- (B_{18})

and $$\left[\frac{\partial\left(\Delta G^0\right)}{\partial T}\right]_P = -\Delta S^0$$ --------------------- (B_{19})

Now, from Eqns. (B_3) and (B_4), we have:

$$\Delta G = \Delta G^0 + RT \ln K_P$$ --------------------- (B_{20})

Or at equilibrium:

$$\Delta G = 0 = \Delta G^0 + RT \ln K_P$$ --------------------- (B_{21})

or $$\Delta G^0 = -RT \ln K_P$$ --------------------- (B_{22})

Plugging Eq. (B_{22}) into Eqns. (B_{18}) and (B_{19}), we obtain;

$$\frac{\partial\left(\ln K_P\right)}{\partial T} = \frac{\Delta H^0}{T^2}$$ --------------------- (B_{23})

and $T\frac{\partial(\ln K_P)}{\partial T}+\ln K_P=\frac{\Delta S^0}{R}$ --------------------- (B_{24})

Plugging Eq. (C_{24}) into Eq. (C_{23}), we obtain:

$$\ln K_P=-\frac{\Delta H^0}{RT}+\frac{\Delta S^0}{R}$$ --------------------- (B_{25})

Now, $K_P=\frac{1}{\frac{P_{H_2}}{(P_{H_2})^{\mathrm{Re}\,f}}}$ --------------------- (B_{26})

$$\ln\frac{P_{H_2}}{(P_{H_2})^{\mathrm{Re}\,f}}=\frac{\Delta H^0}{RT}-\frac{\Delta S^0}{R}$$ --------------------- (B_{27})

Note that, Eq. (B_{27}) is of the form:

$$\ln\left(\frac{P_{H_2}}{P_{H_2}^{\mathrm{Re}\,f}}\right)=\frac{\alpha_1}{T}+\alpha_2$$ --------------------- (B_{28})