Supporting Information Available.

Gibbs energy with respect to temperature during reduction of CO_2 can be predicted as follows:

The Gibbs energy for a closed system,

$dG = VdP - SdT$, at constant pressure (dP = 0) (Eq. 1)

$dG = -SdT$, or $\left(\frac{\partial G}{\partial T}\right)_P = -S$ (Eq. 2)

where V = volume, P = pressure, G = Gibbs energy, T = Kelvin temperature (K), S = entropy

From the Gibbs energy (G = H-TS) for a closed system, divide by T, and rearrange

$$\frac{G}{T} = \frac{H + T\left(\frac{\partial G}{\partial T}\right)_P}{T}, \text{ because } \left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \text{(Eq. 3)}$$

where H = enthalpy

From Eq.3, the change of G/T ratio with respect to T found with quotient rule (Eq.4-1),

$$\left[\partial\left(\frac{G}{T}\right)/\partial T\right]_p = \frac{T\left(\frac{\partial G}{\partial T}\right)_p - H - T\left(\frac{\partial G}{\partial T}\right)_p}{T^2} = -\frac{H}{T^2}, \text{ (Gibbs-Helmholtz equation)} \qquad \text{(Eq. 4)}$$

$$\frac{d}{dx} f(x) = f'(x) = \frac{g'(x)\,h(x) - g(x)\,h'(x)}{h(x)^2}, \text{ where } f(x) = \frac{g(x)}{h(x)} \qquad \text{(Eq. 4-1)}$$

Rearrange Eq.4,

$$d\left(\frac{\Delta G}{T}\right)_P = -\frac{\Delta H}{T^2} dT \qquad \text{(Eq. 5)}$$

then integrate Eq.5 with respect to T,

$$\int_{T_1}^{T_2} d\left(\frac{\Delta_r G}{T}\right) = -\Delta_r H^0 \int_{T_1}^{T_2} \frac{1}{T^2} dT \text{ (assume } \Delta_r H^0 \text{ independent of T)} \qquad \text{(Eq. 6) *}$$

$\Delta_r H^0$ and $\Delta_r G^0$ at 298K, 1atm can calculate using Table 1, A-Eq.6-1 and 2

$$\Delta_r H^0 = \sum \gamma \Delta_f \overline{H}^0 \text{(products) - } \sum \gamma \Delta_f \overline{H}^0 \text{(reactants)} \qquad \text{(Eq. 6-1)}$$

$$\Delta_r G^0 = \sum \gamma \Delta_f \overline{G}^0 \text{(products) - } \sum \gamma \Delta_f \overline{G}^0 \text{(reactants)} \qquad \text{(Eq. 6-2)}$$

Finally, the change of Gibbs energy with respect to T can calculate from Eq.6.

$$\left(\frac{\Delta_r G^0}{T}\right)_{T_2} - \left(\frac{\Delta_r G^0}{T}\right)_{T_1} = \Delta_r H^0 \left(\frac{1}{T_2} - \frac{1}{T_1}\right), \text{ or}$$

$$\left(\frac{\Delta_r G^0}{T}\right)_{T2} = \left(\frac{\Delta_r G^0}{T}\right)_{T1} + \Delta_r H^0 \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \text{(Eq. 7)}$$

Table 1. The standard molar enthalpy ($\Delta_f \overline{H}^0$) and Gibbs energies ($\Delta_f \overline{G}^0$) of formation[20]

	$\Delta_f \overline{H}^0$ (KJ·mol^{-1})	$\Delta_f \overline{G}^0$ (KJ·mol^{-1})
$H_{2(g)}$	0	0
$H_2O_{(g)}$	-241.8	-228.6
$C_{graphite}$	0	0
$CH_{4(g)}$	-74.85	-50.79
$CO_{(g)}$	-110.5	-137.3
$CO_{2(g)}$	-393.5	-394.4
$Fe_{(s)}$	0	0
$Zn_{(s)}$	0	0
$ZnO_{(s)}$	-348.3	-318.3