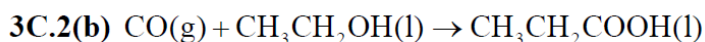# Exercise
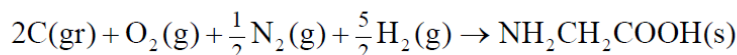
**3C.2(b)** $CO(g) + CH_3CH_2OH(l) \rightarrow CH_3CH_2COOH(l)$

$$\Delta_r H^{\ominus} = \sum_{\text{Products}} \nu \Delta_f H^{\ominus} - \sum_{\text{Reactants}} \nu \Delta_f H^{\ominus} \quad [2C.5]$$

$$= -510.7\,\text{kJ mol}^{-1} - (-277.69\,\text{kJ mol}^{-1}) - (-110.53\,\text{kJ mol}^{-1})$$
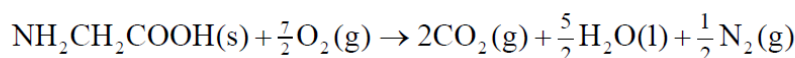
$$= -122.5\,\text{kJ mol}^{-1}$$

$$\Delta_r S^{\ominus} = \sum_{\text{Products}} \nu S_m^{\ominus} - \sum_{\text{Reactants}} \nu S_m^{\ominus} \quad [3B.2]$$

$$= 191.0\,\text{J K}^{-1}\,\text{mol}^{-1} - 160.7\,\text{J K}^{-1}\,\text{mol}^{-1} - 197.67\,\text{J K}^{-1}\,\text{mol}^{-1}$$

$$= -167.4\,\text{J K}^{-1}\,\text{mol}^{-1}$$

$$\Delta_r G^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus}$$

$$= -122.5\,\text{kJ mol}^{-1} - (298\,\text{K}) \times (-167.4\,\text{J K}^{-1}\,\text{mol}^{-1})$$

$$= \boxed{-72.6\,\text{kJ mol}^{-1}}$$

**3C.5(b)** The formation reaction of glycine is

$$2C(gr) + O_2(g) + \frac{1}{2}N_2(g) + \frac{5}{2}H_2(g) \rightarrow NH_2CH_2COOH(s)$$

The combustion reaction is

$$NH_2CH_2COOH(s) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + \frac{5}{2}H_2O(l) + \frac{1}{2}N_2(g)$$

$$\Delta_c H = 2\Delta_f H^{\ominus}(CO_2,g) + \frac{5}{2}\Delta_f H^{\ominus}(H_2O,l) - \Delta_f H^{\ominus}(NH_2CH_2COOH(s))$$

$$\Delta_f H^{\ominus}(NH_2CH_2COOH(s)) = 2\Delta_f H^{\ominus}(CO_2,g) + \frac{5}{2}\Delta_f H^{\ominus}(H_2O,l) - \Delta_c H(NH_2CH_2COOH(s))$$

$$= -2 \times 393.51\,\text{kJ mol}^{-1} + (\frac{5}{2}) \times (-285.83\,\text{kJ mol}^{-1}) - (-969\,\text{kJ mol}^{-1})$$

$$= -532.\overline{6}\,\text{kJ mol}^{-1}$$

$$\Delta_f S^{\ominus} = S_m^{\ominus}(NH_2CH_2COOH(s)) - 2 \times S_m^{\ominus}(C,gr) - S_m^{\ominus}(O_2,g) - \frac{1}{2} \times S_m^{\ominus}(N_2,g) - \frac{5}{2} \times S_m^{\ominus}(H_2,g)$$

$$= 103.5\,\text{J K}^{-1}\,\text{mol}^{-1} - 2 \times 5.740\,\text{J K}^{-1}\,\text{mol}^{-1} - (205.138\,\text{J K}^{-1}\,\text{mol}^{-1})$$

$$- \frac{1}{2} \times 191.61\,\text{J K}^{-1}\,\text{mol}^{-1} - \frac{5}{2} \times (130.684\,\text{J K}^{-1}\,\text{mol}^{-1})$$

$$= -535.\overline{63}\,\text{J K}^{-1}\,\text{mol}^{-1}$$

$$\Delta_f G^{\ominus} = \Delta_f H^{\ominus} - T\,\Delta_f S^{\ominus}$$

$$= -532.\overline{6}\,\text{kJ mol}^{-1} - (298.15\,\text{K}) \times (-535.\overline{63}\,\text{J K}^{-1}\,\text{mol}^{-1})$$

$$= \boxed{-373\,\text{kJ mol}^{-1}}$$

**3D.2(b)** $\left(\dfrac{\partial G}{\partial T}\right)_p = -S$ [3D.8]; hence $\left(\dfrac{\partial G_f}{\partial T}\right)_p = -S_f$, and $\left(\dfrac{\partial G_i}{\partial T}\right)_p = -S_i$

$$\Delta S = S_f - S_i = -\left(\dfrac{\partial G_f}{\partial T}\right)_p + \left(\dfrac{\partial G_i}{\partial T}\right)_p = -\left(\dfrac{\partial (G_f - G_i)}{\partial T}\right)_p$$

$$= -\left(\dfrac{\partial \Delta G}{\partial T}\right)_p = -\dfrac{\partial}{\partial T}\left(-73.1\,\text{J} + 42.8\,\text{J} \times \dfrac{T}{\text{K}}\right)$$

$$= \boxed{-42.8\,\text{J K}^{-1}}$$

# Problem

**3D.2**  The Gibbs–Helmholtz equation [3D.9] may be recast into an analogous equation involving $\Delta G$ and $\Delta H$, since

$$\left(\dfrac{\partial \Delta G}{\partial T}\right)_p = \left(\dfrac{\partial G_f}{\partial T}\right)_p - \left(\dfrac{\partial G_i}{\partial T}\right)_p$$

and $\quad \Delta H = H_f - H_i$

Thus, $\quad \left(\dfrac{\partial}{\partial T}\dfrac{\Delta_r G^{\ominus}}{T}\right)_p = -\dfrac{\Delta_r H^{\ominus}}{T^2}$

$$d\left(\dfrac{\Delta_r G^{\ominus}}{T}\right) = \left(\dfrac{\partial}{\partial T}\dfrac{\Delta_r G^{\ominus}}{T}\right)_p dT[\text{constant pressure}] = -\dfrac{\Delta_r H^{\ominus}}{T^2}dT$$

$$\Delta\left(\dfrac{\Delta_r G^{\ominus}}{T}\right) = -\int_{T_c}^{T} \dfrac{\Delta_r H^{\ominus}\,dT}{T^2}$$
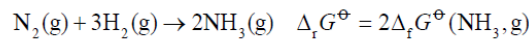
$$\approx -\Delta_r H^{\ominus}\int_{T_c}^{T}\dfrac{dT}{T^2} = \Delta_r H^{\ominus}\left(\dfrac{1}{T} - \dfrac{1}{T_c}\right) \quad [\Delta_r H^{\ominus} \text{ assumed constant}]$$

Therefore, $\quad \dfrac{\Delta_r G^{\ominus}(T)}{T} - \dfrac{\Delta_r G^{\ominus}(T_c)}{T_c} \approx \Delta_r H^{\ominus}\left(\dfrac{1}{T} - \dfrac{1}{T_c}\right)$

$$\Delta_r G^{\ominus}(T) = \dfrac{T}{T_c}\Delta_r G^{\ominus}(T_c) + \left(1 - \dfrac{T}{T_c}\right)\Delta_r H^{\ominus}(T_c)$$
and so
$$= \tau\Delta_r G^{\ominus}(T_c) + (1 - \tau)\Delta_r H^{\ominus}(T_c) \quad \text{where} \quad \tau = \dfrac{T}{T_c}$$

For the reaction

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \quad \Delta_r G^{\ominus} = 2\Delta_f G^{\ominus}(NH_3, g)$$

**(a)**  At 500 K, $\tau = \dfrac{500}{298} = 1.67\overline{8}$,

$$\Delta_r G^{\ominus}(500\,\text{K}) = \{(1.67\overline{8}) \times 2 \times (-16.45) + (1 - 1.67\overline{8}) \times 2 \times (-46.11)\}\,\text{kJ mol}^{-1}$$
so
$$\boxed{= -7\,\text{kJ mol}^{-1}}$$

**(b)**  At 1000 K, $\tau = \dfrac{1000}{298} = 3.35\overline{6}$,

$$\Delta_r G^{\ominus}(1000\,\text{K}) = \{(3.35\overline{6}) \times 2 \times (-16.45) + (1 - 3.35\overline{6}) \times 2 \times (-46.11)\}\,\text{kJ mol}^{-1}$$
so
$$\boxed{= +107\,\text{kJ mol}^{-1}}$$

**3D.6**   **(a)**   $\alpha = \left(\dfrac{1}{V}\right) \times \left(\dfrac{\partial V}{\partial T}\right)_P ;\qquad \kappa_T = -\left(\dfrac{1}{V}\right) \times \left(\dfrac{\partial V}{\partial p}\right)_T$

(1)   $\left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial p}{\partial T}\right)_V$   [Maxwell relation]

$\left(\dfrac{\partial p}{\partial T}\right)_V = -\left(\dfrac{\partial V}{\partial T}\right)_P \left(\dfrac{\partial p}{\partial V}\right)_T$ [Euler chain relation, *Mathematical Background* 2]

$= -\dfrac{\left(\dfrac{\partial V}{\partial T}\right)_P}{\left(\dfrac{\partial V}{\partial p}\right)_T}$ [reciprocal identity, *Mathematical Background* 2]

$= -\dfrac{\left(\dfrac{1}{V}\right)\left(\dfrac{\partial V}{\partial T}\right)_P}{\left(\dfrac{1}{V}\right)\left(\dfrac{\partial V}{\partial p}\right)_T} = \boxed{+\dfrac{\alpha}{\kappa_T}}$

$\left(\dfrac{\partial V}{\partial S}\right)_P = \left(\dfrac{\partial T}{\partial p}\right)_S$   [Maxwell relation]

$\left(\dfrac{\partial T}{\partial p}\right)_S = -\left(\dfrac{\partial T}{\partial S}\right)_P \left(\dfrac{\partial S}{\partial p}\right)_T$ [Euler chain] $= -\dfrac{\left(\dfrac{\partial S}{\partial p}\right)_T}{\left(\dfrac{\partial S}{\partial T}\right)_P}$ [reciprocal]

First treat the numerator:

$\left(\dfrac{\partial S}{\partial p}\right)_T = -\left(\dfrac{\partial V}{\partial T}\right)_P$ [Maxwell relation] $= -\alpha V$

As for the denominator, at constant $p$

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_p \mathrm{d}T \quad \text{and} \quad \mathrm{d}S = \frac{\mathrm{d}q_{\mathrm{rev}}}{T} = \frac{\mathrm{d}H}{T} = \frac{C_p\,\mathrm{d}T}{T} \quad [\mathrm{d}q_p = \mathrm{d}H]$$

Therefore, $\left(\dfrac{\partial S}{\partial T}\right)_p = \dfrac{C_p}{T}$ and $\left(\dfrac{\partial V}{\partial S}\right)_p = \boxed{\dfrac{\alpha TV}{C_p}}$

(2) $\left(\dfrac{\partial p}{\partial S}\right)_V = -\left(\dfrac{\partial T}{\partial V}\right)_S$ [Maxwell relation]

$$-\left(\frac{\partial T}{\partial V}\right)_S = \frac{1}{\left(\dfrac{\partial S}{\partial T}\right)_V\left(\dfrac{\partial V}{\partial S}\right)_T} \text{[Euler chain]} = \frac{\left(\dfrac{\partial S}{\partial V}\right)_T}{\left(\dfrac{\partial S}{\partial T}\right)_V} \text{[reciprocal]}$$

$$= \frac{\left(\dfrac{\partial p}{\partial T}\right)_V}{\left(\dfrac{\partial S}{\partial U}\right)_V\left(\dfrac{\partial U}{\partial T}\right)_V} \text{[Maxwell relation]} = \frac{-\left(\dfrac{\partial p}{\partial V}\right)_T\left(\dfrac{\partial V}{\partial T}\right)_p}{\left(\dfrac{\partial S}{\partial U}\right)_V\left(\dfrac{\partial U}{\partial T}\right)_V}\text{[Euler chain relation]}$$

$$= \frac{-\left(\dfrac{\partial V}{\partial T}\right)_p\left(\dfrac{\partial U}{\partial S}\right)_V}{\left(\dfrac{\partial V}{\partial p}\right)_T\left(\dfrac{\partial U}{\partial T}\right)_V} \text{[reciprocal identity, twice]} = \boxed{\dfrac{\alpha T}{\kappa_T C_V}} \quad \left[\left(\dfrac{\partial U}{\partial S}\right)_V = T\right]$$

**(b)** $\quad \mu_J = \left(\dfrac{\partial T}{\partial V}\right)_U \quad C_V = \left(\dfrac{\partial U}{\partial T}\right)_V$

$$\mu_J C_V = \left(\frac{\partial T}{\partial V}\right)_U\left(\frac{\partial U}{\partial T}\right)_V = \frac{-1}{\left(\dfrac{\partial V}{\partial U}\right)_T}\text{[Euler chain relation]}$$

$$= -\left(\frac{\partial U}{\partial V}\right)_T \text{[reciprocal identity]} = p - T\left(\frac{\partial p}{\partial T}\right)_V \text{[3D.6]}$$

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{-1}{\left(\dfrac{\partial T}{\partial V}\right)_p\left(\dfrac{\partial V}{\partial p}\right)_T}\text{[Euler chain]} = \frac{-\left(\dfrac{\partial V}{\partial T}\right)_p}{\left(\dfrac{\partial V}{\partial p}\right)_T} = \frac{\alpha}{\kappa_T}$$

Therefore, $\boxed{\mu_J C_V = p - \dfrac{\alpha T}{\kappa_T}}$

**3D.10** The Gibbs–Helmholtz equation is

$$\frac{\partial}{\partial T}\left(\frac{\Delta G}{T}\right) = -\frac{\Delta H}{T^2}$$

so for a small temperature change

$$\Delta\left(\frac{\Delta_r G^{\ominus}}{T}\right) = \frac{\Delta_r H^{\ominus}}{T^2}\,\Delta T \quad \text{and} \quad \frac{\Delta_r G_2^{\ominus}}{T_2} = \frac{\Delta_r G_1^{\ominus}}{T_1} - \frac{\Delta_r H^{\ominus}}{T^2}\,\Delta T$$

so $\quad \displaystyle\int d\frac{\Delta_r G^{\ominus}}{T} = -\int \frac{\Delta_r H^{\ominus} dT}{T^2} \quad \text{and} \quad \frac{\Delta_r G_{190}^{\ominus}}{T_{190}} = \frac{\Delta_r G_{220}^{\ominus}}{T_{220}} + \Delta_r H^{\ominus}\left(\frac{1}{T_{190}} - \frac{1}{T_{220}}\right)$

$$\Delta_r G_{190}^{\ominus} = \Delta_r G_{220}^{\ominus}\frac{T_{190}}{T_{220}} + \Delta_r H^{\ominus}\left(1 - \frac{T_{190}}{T_{220}}\right)$$

For the monohydrate

$$\Delta_r G_{190}^{\ominus} = (46.2\,\text{kJ mol}^{-1})\times\left(\frac{190\,\text{K}}{220\,\text{K}}\right) + (127\,\text{kJ mol}^{-1})\times\left(1 - \frac{190\,\text{K}}{220\,\text{K}}\right),$$

$$\Delta_r G_{190}^{\ominus} = \boxed{57.2\,\text{kJ mol}^{-1}}$$

For the dihydrate

$$\Delta_r G_{190}^{\ominus} = (69.4\,\text{kJ mol}^{-1})\times\left(\frac{190\,\text{K}}{220\,\text{K}}\right) + (188\,\text{kJ mol}^{-1})\times\left(1 - \frac{190\,\text{K}}{220\,\text{K}}\right),$$

$$\Delta_r G_{190}^{\ominus} = \boxed{85.6\,\text{kJ mol}^{-1}}$$

For the trihydrate

$$\Delta_r G_{190}^{\ominus} = (93.2\,\text{kJ mol}^{-1})\times\left(\frac{190\,\text{K}}{220\,\text{K}}\right) + (237\,\text{kJ mol}^{-1})\times\left(1 - \frac{190\,\text{K}}{220\,\text{K}}\right),$$

$$\Delta_r G_{190}^{\ominus} = \boxed{112.8\,\text{kJ mol}^{-1}}$$