

## Solutions Problem set 2, Thermodynamics 1

### Exercise Maths 2

- a)  $\int_{T_1}^{T_2} \alpha \, dT = \alpha(T_2 - T_1)$ ,
- b)  $\int_{x_1}^{x_2} \frac{1}{p} \, dx = \frac{1}{p}(x_2 - x_1)$ ,
- c)  $\int_{y_1}^{y_2} (g + hy) \, dy = g(y_2 - y_1) + \frac{h}{2}(y_2^2 - y_1^2)$ ,
- d)  $\int_{z_1}^{z_2} \frac{C}{z} \, dz = C \ln \frac{z_2}{z_1}$ ,
- e)  $\frac{dU}{dT} = \frac{d}{dT} \left( \frac{3}{2}nRT \right) = \frac{3}{2}nR$ , so  $dU = \frac{3}{2}nRdT$ .

### Exercise 6

Given is  $n = 3$  moles,  $p = 3.25$  atm,  $T_1 = 260$  K,  $T_2 = 285$  K and  $C_p = 29.4$  JK<sup>-1</sup>mol<sup>-1</sup>. The heat capacity is given by  $C_p = \frac{dq_p}{dT}$ , which gives us  $dq = C_p dT$ . Integrating on both sides,  $\int dq = \int_{T_1}^{T_2} C_p dT$ , results in  $q = C_p(T_2 - T_1) = 29.4$  J K<sup>-1</sup>mol<sup>-1</sup> · (285 K - 260 K) = 735 J mol<sup>-1</sup>. In our case we have  $n = 3$  moles, so  $q = 3 \cdot 735$  J mol<sup>-1</sup> = 2205 J.

We know that at constant  $p$ ,  $dH = dq_p$  so the change in enthalpy is  $\Delta H = 2205$  J.

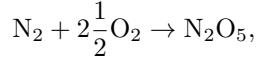
To calculate the change in the internal energy, we note that some  $pV$  work will be done on expansion, therefore not all heat supplied will raise the internal energy of the sample. So  $\Delta U < q$  or in other words  $\Delta U < \Delta H$ .  $H = U + pV$ , so  $\Delta H = \Delta U + \Delta(pV)$ . Therefore  $\Delta U = \Delta H - \Delta(pV) = \Delta H - \Delta(nRT) = \Delta H - nR\Delta T = 2205 \text{ J} - 3 \cdot 8.314 \text{ JK}^{-1}\text{mol}^{-1} \cdot (285 \text{ K} - 260 \text{ K}) = 2205 \text{ J} - 623.55 \text{ J} = 1581 \text{ J}$

### Exercise 7

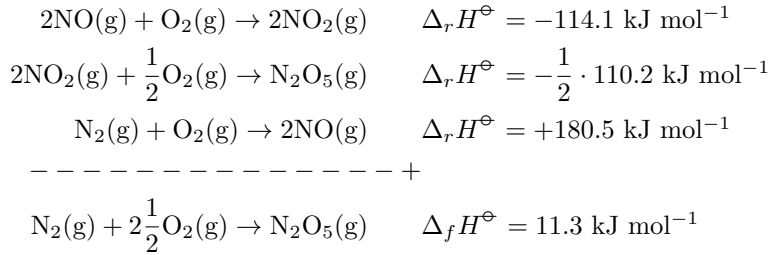
- a) For a bomb calorimeter the volume is constant,  $dV = 0$ , and hence the expansion work is also 0. It then follows from the 1st law that  $\Delta U = q$ , and  $C = q/\Delta T$  can thus be written as  $C = \Delta U/\Delta T$ . As we have  $0.825$  g /  $122$  g mol<sup>-1</sup> =  $0.00676$  moles of benzoic acid,  $C_{V,bomb} = \frac{q_{calorimeter}}{\Delta T} = \frac{+3251 \cdot 10^3 \cdot 0.00676}{1.94} = 11.33$  kJ K<sup>-1</sup>. Note that  $q_{calorimeter} = -\Delta U$  reaction!
- b) **Fumaric acid:**  
 $n = 0.498$  g /  $116$  g mol<sup>-1</sup> =  $0.00429$  moles and  $q = C\Delta T = 11.33 \cdot 10^3 \cdot 0.507 = 5743$  J. So the heat uptake of the calorimeter is  $5743 / 0.00429 = 1338$  kJ mol<sup>-1</sup>. So  $\Delta_{comb}U = -1338$  kJ mol<sup>-1</sup>.  
**Maleic acid:**  
 $n = 0.509$  g /  $116$  g mol<sup>-1</sup> =  $0.00439$  moles and  $q = C\Delta T = 11.33 \cdot 10^3 \cdot 0.528 = 5981.3$  J. So the heat uptake of the calorimeter is  $5981.3 / 0.00439 = 1363$  kJ mol<sup>-1</sup>. So  $\Delta_{comb}U_{is} = -1363$  kJ mol<sup>-1</sup>.
- c)  $H = U + pV$ , so  $\Delta_{comb}H = \Delta_{comb}U + \Delta(nRT)$ . Note that we ignore the small change in temperature as its contribution to  $\Delta H$  is very small compared to the contribution due to  $\Delta n$ .  
**Fumaric acid:** Filling in the values:  $-1338 \cdot 10^3 + (4 - 3)(8.314)(298) = -1336$  kJ/mol.  
**Maleic acid:** Filling in the values:  $-1363 \cdot 10^3 + n_{gas}(8.314)(298) = -1361$  kJ/mol.
- d) **Fumaric acid:**  $\Delta_f H = 4 \cdot (\Delta_f H_{CO_2}) + 2 \cdot (\Delta_f H_{H_2O}) - \Delta_{comb}H = -809.6$  kJ/mol.  
**Maleic acid:**  $\Delta_f H = 4 \cdot (\Delta_f H_{CO_2}) + 2 \cdot (\Delta_f H_{H_2O}) - \Delta_{comb}H = -784.6$  kJ/mol.
- e) Fumaric acid is more stable due to less steric repulsion in trans conformation.

## Exercise 8

The reaction corresponding to the enthalpy of formation of  $\text{N}_2\text{O}_5$ ,



can be obtained by the addition of the following reactions:



Hence,  $\Delta_f H^\ominus$  of  $\text{N}_2\text{O}_5$  is thus  $180.5 - 114.1 - \frac{110.2}{2} = +11.3 \text{ kJ/mol}$ .

## Exercise 9

From the definition of the heat capacity at constant pressure,  $C_p = \left(\frac{\partial H}{\partial T}\right)_p$ , we get  $dH = C_p dT$ . Integrating on both sides,  $\int_{T_1}^{T_2} dH = \int_{T_1}^{T_2} C_p dT$ , results in  $H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_p dT$ . Combining this with the expression for the heat capacity,  $C_p = A + BT$ , leads to  $H(T_2) = H(T_1) + \int_{T_1}^{T_2} (A + BT) dT = H(T_1) + [AT + \frac{1}{2}BT^2]_{T_1}^{T_2} = H(T_1) + A(T_2 - T_1) + \frac{1}{2}B(T_2^2 - T_1^2)$ . Note that this is true for each component.

The reaction enthalpy is then given by  $\Delta_r H(T_2) = \Delta_r H(T_1) + \Delta_r A(T_2 - T_1) + \frac{\Delta_r B}{2}(T_2^2 - T_1^2)$ . The reaction under consideration is  $\frac{1}{2}\text{N}_2(\text{g}) + \frac{3}{2}\text{H}_2(\text{g}) \rightarrow \text{NH}_3$ , with a  $\Delta_r H$  of  $-46.11 \text{ kJ/mol}$  at  $298 \text{ K}$ .

With the values in the table we can calculate A and B, we find

$$\begin{aligned} \Delta_r A &= 29.75 - \frac{3}{2}(27.28) - \frac{1}{2}(28.58) = -25.46 \\ \Delta_r B &= (25.1 - \frac{3}{2}(3.26) - \frac{1}{2}(3.77)) \cdot 10^{-3} = 18.325 \cdot 10^{-3} \end{aligned}$$

Now the formula derived above can be filled in.  $\Delta_r H(1000 \text{ K}) = \Delta_r H(298 \text{ K}) + \Delta_r A(1000 - 298) + \frac{\Delta_r B}{2}(1000^2 - 298^2) = -46.11 \cdot 10^3 - 25.46(702) + \frac{18.325 \cdot 10^{-3}}{2}(911196) = -55.6 \text{ kJ/mol}$

## Exercise 10

We are dealing with an adiabatic process thus  $dq = 0$ , therefore  $dU = dw$ . Additionally, this is a reversible process,  $p_{ex} = p$ , so  $dw = -pdV$ .

- From the definition of the heat capacity at constant volume,  $C_v = \left(\frac{\partial U}{\partial T}\right)_V$ , we write  $dU = C_v dT$ . As  $dU = dw = -pdV$ , we obtain  $C_v dT = -pdV = -nRT \frac{dV}{V}$ . As we are dealing with a perfect gas, the perfect gas law applies ( $pV = nRT$ ), which can be subbed in for  $p$ . Rewriting and integrating on both sides then gives  $\int_{T_i}^{T_f} \frac{C_v}{T} dT = -\int_{V_i}^{V_f} \frac{nR}{V} dV$ . So  $C_v \ln\left(\frac{T_f}{T_i}\right) = -nR \ln\left(\frac{V_f}{V_i}\right)$ . Filling in the known values we obtain  $\frac{3}{2}R \ln\left(\frac{T_f}{298}\right) = -R \ln(2)$ , which leads to a final temperature of  $T_f = 187.7 \text{ K}$ .
- For the work we use  $dw = dU = C_v dT$ . Integration gives us  $w = C_v \Delta T$ . Filling in the values then gives  $w = \frac{3}{2}R(187.7 - 298) = -1376 \text{ J}$ .