

CHEM 3410: Physical Chemistry I — Fall 2008

### Homework 3 — Solutions

1. We defined enthalpy as  $H \equiv U + PV$ . We can then write the change in enthalpy as:

$$\Delta H = \Delta U + \Delta(PV)$$

But for an ideal gas,  $PV = nRT$ . Substituting this in to the above equation yields:

$$\Delta H = \Delta U + \Delta(nRT)$$

At constant temperature this further simplifies to:

$$\Delta H = \Delta U + \Delta nRT = 9400 \text{ J/mole} + (0.27 \text{ mol})(8.314 \text{ J/mole} \cdot \text{K})(300 \text{ K})$$

$$\boxed{\Delta H = 10.1 \text{ kJ}}$$

2. At constant pressure,  $\Delta H = q$  and we can solve for them both using the heat capacity:

$$\Delta H = q = \int_{T_i}^{T_f} nC_p dT = R \int_{348}^{1623} 3.093 + 6.967 \times 10^{-3}T - 45.81 \times 10^{-7}T^2 + 1.035 \times 10^{-9}T^3$$

Notice I wrote the integral ignoring the units of temperature (K). This is not a smart move, but it makes the writing of the solution a little easier.

$$\Delta H = q = R \left[ 3.093T + 6.967 \times 10^{-3} \frac{T^2}{2} - 45.81 \times 10^{-7} \frac{T^3}{3} + 1.035 \times 10^{-9} \frac{T^4}{4} \right]_{348}^{1623}$$

Evaluating the term in the brackets at the final temperature minus the initial temperature (as indicated with the notation) we get:

$$\boxed{\Delta H = q = 66.6 \text{ kJ}}$$

We can find the change in internal energy since (1) the number of moles remains the same and (2) we know the temperature change and it is an ideal gas:

$$\Delta U = \Delta H - \Delta(PV) = \Delta H - nR\Delta T = 66.6 \times 10^3 \text{ J} - (1)(8.314 \text{ J/mol} \cdot \text{K})(1623 - 348 \text{ K})$$

$$\boxed{\Delta U = 56.0 \text{ kJ}}$$

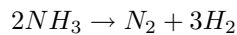
Since we now know the internal energy change and the heat flow, we can find the work done using the first law:

$$w = \Delta U - q = 56.0 \text{ kJ} - 66.6 \text{ kJ}$$

$$\boxed{w = -10.6 \text{ kJ}}$$

The sign of our answer does make sense since the gas is being heated and is expanding, thus work is being done by the gas and the sign of  $w$  should be negative.

3. (a) The reaction at 1200K is



$P = \frac{nRT}{V}$ , T and V are constant but  $n$  increases by a factor of 2 in the reaction. Therefore

$$P_f = 2P_i \rightarrow \boxed{P_f = 20 \text{ atm}}$$

(b) Heat flow

The system is under constant volume ( $dV = 0$ ) so  $W = 0$  and

$$\Delta U = Q$$

We can compute  $U$  from  $H$  because

$$U = H - PV$$

$$\Delta U = \Delta H - \Delta(PV) = \Delta H - \Delta(nRT) = \Delta H - RT\Delta n$$

$$\Delta H = 87 \frac{\text{kJ}}{\text{mole}} \text{ and } \Delta n = 2 \text{ moles}$$

$$\Delta U = 87000 \frac{\text{J}}{\text{mole}} - (2) \left( 8.314 \frac{\text{J}}{\text{mole} \cdot \text{K}} \right) (1200\text{K})$$

$$\Delta U = \boxed{Q = 67046 \frac{\text{J}}{\text{mole}}}$$

(c) System is adiabatic and under constant volume  $\implies \Delta U = 0$

So,

$$\Delta U_{\text{reaction}} + \int_{1200}^{T_a} (C_{v,N_2} + 3C_{v,H_2}) dT = 0$$

$$T_a = 1200 - \frac{\Delta U_{\text{reaction}}}{C_{v,N_2} + 3C_{v,H_2}}$$

use  $c_p - c_v = R$

$$T_a = 1200 - \frac{67046 \frac{\text{J}}{\text{mole}}}{4 * 24.686 \frac{\text{J}}{\text{mole} \cdot \text{K}}}$$

$$\boxed{T_a = 521 \text{ K}}$$

The system cools down which is expected given that the reaction is endothermic.