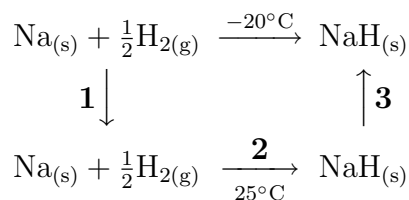


# Chemistry 2740 Spring 2009 Test 1 Solutions

1. In the following, words in parentheses are optional
  - (a) molar (internal) energy (change) of combustion
  - (b) constant-volume heat capacity
  - (c) specific enthalpy (change) of reaction
2.  $\Delta H = \Delta U + \Delta(pV)$ . For reactions in solution,  $\Delta(pV)$  is very small, so  $\Delta U \approx \Delta H$ .
3. Suppose that we expand a gas isothermally from  $(p_1, V_1)$  to  $(p_2, V_2)$ . Since  $w = \int_{\mathcal{P}} p_{\text{ext}} dV$ , the work is just the negative of the area under the curve of  $p_{\text{ext}}$  vs  $V$ . Figure 1 sketches the  $pV$  isotherm (solid) as well as two possible paths connecting the initial and final states. We can immediately see that the area under paths connecting two states need not be the same, and therefore that work is path-dependent.
4.  $\Delta U = q + w$ . The work is given by  $w = - \int_{\mathcal{P}} p_{\text{ext}} dV$ . If there is no change in volume, this integral is clearly zero, so  $\Delta U = q_V$ .
- 5.



$$\begin{aligned}
 \Delta_{(1)}H_m &= \left[ C_{p,m}(\text{Na}) + \frac{1}{2}C_{p,m}(\text{H}_2) \right] \Delta T_1 \\
 &= \left[ 28.2 + \frac{1}{2}(28.82) \text{ J K}^{-1}\text{mol}^{-1} \right] (25 - (-20) \text{ K}) \\
 &= 1.9 \text{ kJ/mol.}
 \end{aligned}$$

$$\Delta_{(2)}H_m = \Delta_f H^\circ(\text{NaH}) = -56.44 \text{ kJ/mol.}$$

$$\begin{aligned}
 \Delta_{(3)}H_m &= C_{p,m}(\text{NaH})\Delta T_3 \\
 &= (36.37 \text{ J K}^{-1}\text{mol}^{-1})(-25 - 20 \text{ K}) \\
 &= -1.6 \text{ kJ/mol.}
 \end{aligned}$$

$$\begin{aligned}
 \therefore \Delta_f H(\text{NaH}, -20^\circ\text{C}) &= 1.9 + (-56.44) + (-1.6) \text{ kJ/mol} \\
 &= -56.2 \text{ kJ/mol.}
 \end{aligned}$$

6. (a) Since the external pressure is constant,  $w = -p_{\text{ext}}\Delta V$ . The big problem is calculating  $\Delta V$ . We know the initial volume (5 mL, or  $5 \times 10^{-6} \text{ m}^3$ ). The number of moles of nitrogen in the balloon is

$$n = \frac{(5 \text{ mL})(0.8086 \text{ g/mL})}{28.013 \text{ 48g/mol}} = 0.14 \text{ mol.}$$

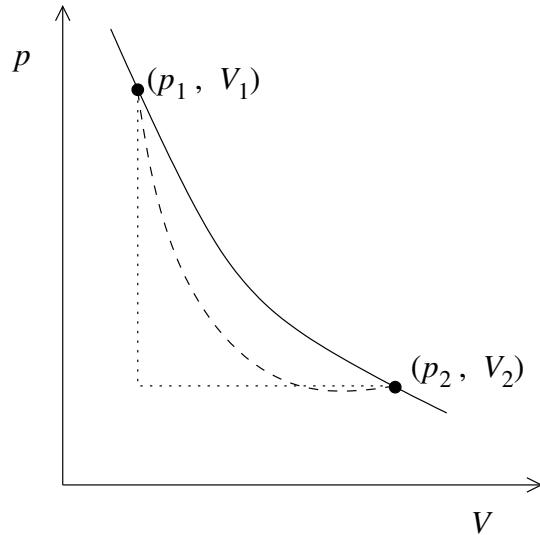


Figure 1:  $pV$  isotherm for a gas (solid), as well as two different paths connecting the initial and final states  $(p_1, V_1)$  and  $(p_2, V_2)$ .

Thus, the final volume of the gas is

$$\begin{aligned}
 V &= \frac{nRT}{p} \\
 &= \frac{(0.14 \text{ mol})(8.314 472 \text{ J K}^{-1} \text{ mol}^{-1})(293.15 \text{ K})}{101 325 \text{ Pa}} \\
 &= 3.5 \times 10^{-3} \text{ m}^3. \\
 \therefore w &= -p_{\text{ext}}\Delta V \\
 &= -(101 325 \text{ Pa})(3.5 \times 10^{-3} - 5 \times 10^{-6} \text{ m}^3) \\
 &= -3.5 \times 10^2 \text{ J}.
 \end{aligned}$$

The negative sign means that work is done by the system on its surroundings.

(b)

$$\begin{aligned}
 \Delta_{\text{vap}}H &= (5.586 \times 10^3 \text{ J/mol})(0.14 \text{ mol}) = 8.1 \times 10^2 \text{ J}. \\
 \Delta_{\text{heat}}H &= n \int_{T_1}^{T_2} C_{p,m} dT \\
 &= n \int_{T_1}^{T_2} (A + BT + CT^2) dT \\
 &= n \left[ AT + \frac{1}{2}BT^2 + \frac{1}{3}CT^3 \right]_{T_1}^{T_2} \\
 &= n \left[ A(T_2 - T_1) + \frac{1}{2}B(T_2^2 - T_1^2) + \frac{1}{3}C(T_2^3 - T_1^3) \right]
 \end{aligned}$$

$$\begin{aligned}
&= (0.14 \text{ mol}) \left[ 28.3 (293.15 - 77.34 \text{ K}) \right. \\
&\quad \left. + \frac{1}{2} (2.54 \times 10^{-3} (293.15^2 - 77.34^2)) \right. \\
&\quad \left. + \frac{1}{3} (5.4 \times 10^{-5} (293.15^3 - 77.34^3)) \right] \\
&= 9.6 \times 10^2 \text{ J.} \\
\therefore q &= \Delta_{\text{vap}} H + \Delta_{\text{heat}} H \\
&= 8.1 \times 10^2 \text{ J} + 9.6 \times 10^2 \text{ J} = 1.77 \times 10^3 \text{ J.}
\end{aligned}$$

(c)

$$\begin{aligned}
\Delta U &= q + w \\
&= 1.77 \times 10^3 + (-3.5 \times 10^2) \text{ J} \\
&= 1.42 \times 10^3 \text{ J} \equiv 1.42 \text{ kJ.}
\end{aligned}$$