Problem Set #1 Chem 471 Fall 1999

Due Friday, 9/17/99, in class.

Show your work. Problem sets will be spot graded. Work must be shown.

\[ R = 0.08206 \text{ liter atm K}^{-1} \text{ mole}^{-1} = 8.314 \text{ J K}^{-1} \text{ mole}^{-1} \]

In the answers that follow, don't just look at the answer, but think about the logic of how you would get to the equations shown. This is critical to success in the course! And it's critical that you come to this understanding on your own!

1. Calculate the work of expansion of an ideal gas from 1L to 4 L under the following conditions (a and b):

   This problem illustrates how you should assess what you know and what you can figure out, but also what you need to know and what you don't. For example, the problem does not tell you explicitly the mass or number of moles of the gas (it is NOT 1 mole). Do you need to know? Not really, as long as parts a and b have the same amount of gas (this is implicit in the question).

   As an aside (this entire paragraph is not necessary for the problem, but you should check that you can easily follow its logic), could you figure out the number of moles, if you needed to? From part (a), no, but from part (b), yes. Remember the ideal gas law: to solve for \( n \), you need \( P, V, \) and \( T \) at either the initial or final condition. From part (b), we know the final \( T \) (25°C), the final pressure (1 atm), and the final volume (4 L). Therefore, \( n=0.164 \) moles. Now knowing this, could we figure out the initial pressure from the info in part (a)? Yes, because we know \( n \) (0.164 mol), \( V \) (1 L), and \( T \) (25°C). Therefore, \( P=4.0 \) atm. Can we figure out the initial pressure from the data in part (b)? This is most readily calculated knowing that \( P_1V_1=P_2V_2 \) (although we could do it the long way too). To solve for \( P_1 \), we need to know \( V_1 \) (1 L), \( P_2 \) (1 atm), and \( V_2 \) (4 L). Therefore, \( P_1=4.0 \) atm (just as we found previously).

   Can you figure out the mass of the gas, from what's given? Answer: no. Why not?

   (a) The gas expands against a constant \( P_{ext} = 1 \text{ atm} \) (ie., you suddenly remove blocks holding the piston); the initial temperature is 25°C. Note that unless otherwise stated, when asked for work, it is the work done ON the system.

\[
w = -\int P_{ext} \, dV
\]

\[
w = -P_{ext} \int dV = -P_{ext} (V_2 - V_1) = -1 \text{ atm}(4 - 1)l = -3l \cdot \text{ atm} = -304 \text{ J}
\]

(b) The expansion is done reversibly, at a constant temperature of 25 °C. The final pressure is 1 atm.

\[
w = -nRT \ln \frac{V_2}{V_1} = -P_2V_2 \ln \frac{V_2}{V_1} = -4l \cdot \text{ atm} \ln \frac{4}{1}
\]

\[
w = -5.55l \cdot \text{ atm} = -562 \text{ J}
\]

(c) Does (a) or (b) do more work?

The reversible expansion does more work: -562 J vs. -304 J.

(d) Show how you convert your answers to parts (a) and (b) from L-atm to Joules.


\[
\frac{1.013 \times 10^5 \text{Nm}^{-2}}{\text{atm}} \times \frac{1 \text{m}^3}{10^3 \text{l}} \times \frac{1 \text{J}}{\text{Nm}} = 101.3 \frac{\text{J}}{\text{l} \cdot \text{atm}}
\]

or use ratio of values for \( R \):

\[
\frac{8.314 \text{JK}^{-1}\text{mole}^{-1}}{0.08206 \text{l} \cdot \text{atmK}^{-1}\text{mole}^{-1}} = 101.3 \frac{\text{J}}{\text{l} \cdot \text{atm}}
\]

2. Tinoco, Sauer, and Wang, 3rd Ed. - Chapter 2, Problem 6
The point here is to understand the use of heat capacity and heats of phase transitions.

q absorbed by 100 g = 0.1 kg of liquid water for the following processes:
(a) 0°C to 100°C at 1 atm: \( q = C_p(T_2 - T_1) = (4.18 \text{ kJ/Kkg})(0.1 \text{ kg})(100-0) \text{K} = 41.8 \text{ kJ} \)
(b) freezing at 0°C, 0.01 atm:
tabulated \( \Delta H \) is for \( P=1 \) atm but \( P \) should have little effect since solids/liquids only
\( q = \Delta H \text{freezing} = (-333.4 \text{ kJ/kg}) (0.1 \text{ kg}) = -33.3 \text{ kJ} \) (negative since giving up heat)
As noted above, the one thing to think about here is the effects of pressure on phase transitions between liquid and solid. To a first approximation, there are not large volume changes on going from liquid to solid. So, it shouldn't make a large difference on the enthalpy of freezing (fusion).
(c) evaporating at 100°C, 1 atm: \( q = \Delta H \text{vaporization} = (2257 \text{ kJ/kg})(0.1 \text{ kg}) = 225.7 \text{ kJ} \)

3. Tinoco, Sauer, and Wang, 3rd Ed. - Chapter 2, Problem 7
1 mole ideal gas: constant \( P_{\text{ext}}=1 \) atm reversible expansion, \( T_1 = 27°C = 300 \text{K}, P_1 = 1 \text{ atm}, T_2 = 327°C = 600 \text{ K}, C_v=20.8 \text{ J/Kmole}, constant

Notes:
(1) can have a reversible expansion against constant \( P \) -- picture slowly heating a balloon such that \( P_{\text{ext}} = P_{\text{int}} \)
every step of the way
(2) note there are 3 possible pressures: \( P_{\text{ext}}=P_1=P_2=1 \) atm -- so you can cancel them in (a)
\( \rightarrow \) but they won't always be equal -- see pb 3b. Thus \( P_{\text{ext}} = \text{constant} \) doesn't necessarily mean constant pressure, ie if \( P_1 \neq P_2 \).
(a) \( w = -P_{\text{ext}}(V_2-V_1) = -P_{\text{ext}}(nRT_2/P_2-nRT_1/P_1) = -nR(T_2-T_1) = -(1 \text{ mole})(8.3145 \text{ J/Kmole})(300 \text{ K}) \)
\( w = -2494 \text{ J} \)
(b) \( \Delta E = q + w = C_p(T_2-T_1) - nR(T_2-T_1) = C_v(T_2-T_1) \)
\( \Delta E = (1 \text{ mole})(20.8 \text{ J/Kmole})(300 \text{ K}) = 6240 \text{ J} \)
\( \Delta H = q_p = \Delta E - w = 6240 \text{ J} + 2494 \text{ J} = 8734 \text{ J} \)
(c) \( q_p = 8734 \text{ J} \)

4. Tinoco, Sauer, and Wang, 3rd Ed. - Chapter 2, Problem 8
1 mole ideal gas, \( T_1 = 300 \text{ K}, P_1 = 10 \text{ atm}, P_2 = 1 \text{ atm} \)
(a) \( T \) constant, reversible: \( P_1V_1 \) to \( P_2V_2 \), reversible means \( P_{\text{ext}} = P_{\text{int}} \) every step of the way.
\( T_2 = 300 \text{ K} \)
\( w_T = -\int P_{\text{ext}} dV = -nRT \ln \frac{V_2}{V_1} \)
\( \frac{V_2}{V_1} = \frac{nRT/P_2}{nRT/P_1} = \frac{P_1}{P_2} = 10 \)
\( w_T = -(1 \text{ mole})(8.3145 \text{ J/Kmole})(300 \text{ K}) \ln (10) = -5.7 \text{ kJ/mole} \)
since ideal gas, \( E \) proportional to \( T \), so for isothermal process \( \Delta E = 0 \)
\[ \Delta H = \Delta E + \Delta (PV) = \Delta E + \Delta (nRT) = 0 \]

\[ q_T = -w_T = 5.7 \text{ kJ/mole} \]

(b) \( q = 0 \), \( P_{\text{ext}} = 1 \text{ atm; } P_1 V_1 T_1 \text{ to } P_2 V_2 T_2 \)

-- note there are 3 pressures in this problem: \( P_1 \) and \( P_2 = P_{\text{ext}} \)

\[ w = -P_{\text{ext}} (V_2 - V_1) \ldots \text{need to calculate } V_1 \text{ and } V_2 \ldots \text{need } T_2 \]

\[ \Delta E = C_v (T_2 - T_1) \text{ (since path-independent, use results of p 39 or 2b above) } \]

\[ \Delta E = w + q = w \]

plug in values for \( P \), units cancel:

\[ -1 \frac{nRT_2}{10} + \frac{nRT_1}{10} = C_v (T_2 - T_1) \]

\[ nRT_2 + C_v T_2 = C_v T_1 + \frac{nRT_1}{10} \]

\[ (nR + C_v) T_2 = C_v T_1 + \frac{10R}{10 + 3R} \cdot T_1 \]

\[ T_2 = \frac{nR}{nR + C_v} \cdot T_1 = \frac{16R/10}{5R/2} \cdot T_1 = \frac{32}{50} (300K) \]

\[ T_2 = 192K \]

\[ \Delta E = C_v (T_2 - T_1) = n(3/2)(R)(300K - 192K) = (1 \text{ mole})(1.5)(8.3145J/Kmole)(108K) = 1347J \]

\[ w = \Delta E = 1347J \]

\[ \Delta H = (C_v + nR)(T_2 - T_1) = n(5/2)(R)(T_2 - T_1) = (1 \text{ mole})(2.5)(8.3145J/Kmole)(108K) = 2245J \]

Note significant difference between \( \Delta H \) and \( \Delta E \) because gas

(c) adiabatic expansion against \( P_{\text{ext}} = 0 \)

\[ q = 0 \text{ because adiabatic, } w = 0 \text{ because no force since } P_{\text{ext}} = 0, \Delta E = q + w = 0. \]

Since ideal gas, both \( \Delta E \) & \( \Delta H \) are proportional to \( \Delta T \), therefore \( \Delta T = 0 \),
then \( \Delta H = 0 \), and \( T_2 = 300K \)

If expansion is against a zero force, then no work is done (intuitive?).

5. Tinoco, Sauer, and Wang, 3rd Ed. - Chapter 2, Problem 10

<table>
<thead>
<tr>
<th>( q )</th>
<th>( w )</th>
<th>( \Delta E )</th>
<th>( \Delta H )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 0</td>
<td>&lt;0 (expansion)</td>
<td>&lt;0 (( \Delta E = q + w ))</td>
<td>&lt;0 (ideal gas ( \Delta H ) &amp; ( \Delta E \propto \Delta T ))</td>
</tr>
<tr>
<td>(b) &gt;0</td>
<td>&lt;0 (expansion)</td>
<td>0 (ideal gas ( \Delta T = 0 ))</td>
<td>0 (ideal gas ( \Delta T = 0 ))</td>
</tr>
<tr>
<td>(c) 0</td>
<td>0 (( P_{\text{ext}} = 0 ))</td>
<td>0 (( \Delta E = q + w ))</td>
<td>0 (( \Delta H = \Delta E + R \Delta T = 0 + 0 ))</td>
</tr>
<tr>
<td>(d) &gt;0</td>
<td>&lt;0 (expansion)</td>
<td>&gt;0 (( \Delta H = q p ))</td>
<td></td>
</tr>
</tbody>
</table>

\[ \Delta n_g \text{ is change in the number of moles of the gas.} \]

(e) <0 (exothermic)  | 0 (\( \Delta V = 0 \))  | <0 (\( \Delta E = q v \))  | <0 [\( \Delta H = \Delta E + \Delta (PV) = \Delta E + n_g RT \text{, both } \Delta E \text{ and } \Delta n_g \text{ are negative } \) ]

6. Tinoco, Sauer, and Wang, 3rd Ed. - Chapter 2, Problem 16

(a) \( \Delta E = q + w \) True in general -- conservation of energy.

(b) \( q = \Delta H \) True for constant pressure & PV work only.

(c) \( C_p = \Delta H / \Delta T \) True for constant pressure, \( C_p \) independent of temperature.

(d) \( \Delta H = \Delta E + \Delta (nRT) \) True for ideal gas.

(e) van der Waals gas equation -- True for real gases over a limited \( P \) & \( T \) range.

(f) \( w = -P_{\text{ex}} \Delta V \) True for PV work only, against constant external pressure.

7. Tinoco, Sauer, and Wang, 3rd Ed. - Chapter 2, Problem 4
This sort of situation arises often with those who are interested in why proteins and nucleic acids fold as they do. The understanding of why different proteins have different folding energetics under various conditions is a very active area of research. Similarly, for DNA and RNA, people are interested in going beyond "AT pairs are weaker than GC pairs" (it's not that simple), and understanding the relationship between energetics and structure.

(a) melting of ice:
q vs T plot = 1 warm ice (slope = Cp (ice), 2 melt ice (vertical line because ΔT = 0), 3 warm water (higher slope than 1 because higher Cp)
Cp vs T plot = 1 const Cp of ice, 2 Cp becomes very large during melting, because can add lots of heat without raising T, 3 new higher Cp of water
Note that Cp is the derivative of the qp vs T curve. Can you see (above and below) that the right plot represents the slope of the first graph?

(b) DNA melting:
q vs T plot -- DNA melts cooperatively, but not as sharply as ice
Cp vs T plot -- Cp is large during melting, because added heat doesn't increase the temperature, then Cp returns to a similar value,
To measure ΔH of the DNA melting transition:
\[ \Delta H = q_p = \int_{T_1}^{T_2} C_p dT \]  To get ΔH for the DNA melting only (not the buffer heating), subtract buffer "baseline"
Cp vs T curve: calculated Cp (DNA only) = Cp (DNA+buffer) - Cp (buffer) -- both measured. Then choose T1 and T2 before and after the transition and integrate the area under the peak in the Cp (DNA only) vs T curve.