April 2008

Advanced Physical Chemistry Problems (V), Thermodynamics (ThermoChemistry)

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I. SYNOPSIS

This is a set of problems that were used near the turn of
the century and which will be lost when the web site they
were on disappears with my demise. Because these prob-
lems are being taken from the web and are being edited,
their statements and the hints/answers offered are sub-
ject to the typical editorial errors that ensue when such
work is undertaken in the vacuum of a non-teaching situ-
ation. Therefore, I claim any errors for myself, and hate
to note that there most likely is no point in contacting
me about them for obvious reasons.

II. THERMODYNAMICS, THE 2nd LAW

1. Calculate the expected adiabatic flame tempera-
ture of hydrogen burned in a stoichiometric amount
of air. Assume \((C_p(O_2(g)) = 29.35 \text{ J/(mol}^\circ\text{K})\). Assume \((C_p(H_2O(g)) = 33.577\) and \(\Delta H_{\text{standard, formation}} = -241.814 \text{ kJ/mol}\). Assume \((C_p(N_2(g)) = 29.12 \text{ J/(mol}^\circ\text{K})\). Assume that the actual 'com-
bustion' takes place at 25\(^\circ\)C. Assume air is 80%
ketone and 20% oxygen.

Answer and/or Hint

We're burning \(H_2\) in air, in a perfect (stoichio-
metric) amount of air. There's a little elementary
chemistry knowledge required now. Air is \(4/5\) \(N_2\)
and \(1/5\) \(O_2\) so if we assume one mole of \(H_2\) then
since we have \(1/2\) mole of \(O_2\), which contains 2
moles \(N_2\) and creates 1 moles of \(H_2O\) according to
the equation

\[H_2(g) + 1 \frac{1}{2} O_2(g) \rightarrow H_2O(g)\]

at 25\(^\circ\)C.

Therefore, the equation

\[-\Delta H_{\text{combustion}} = \int_{273+25}^{273+T_{\text{flame}}} (2C_p(N_2) + C_p(H_2O)) \,dT\]

where the leading sign is because we need to reverse
the heat to make it go into the exiting gases.

As a side note, if the \(C_p\)'s are given as functions of
temperature, we have an interesting nested integral
problem to deal with; something to think about.

2. \(\Delta H_f^0\) of \(HCl(g)\) is -92.31 kJ/mole at 25\(^\circ\)C. The heat
capacities are given in the form:

\[C_p(T) = A + BT + CT^2\]

where \(T\) is in \(^\circ\)K and \(C_p\) is in Joules/(mole K).

<table>
<thead>
<tr>
<th>Name</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_2(g)</td>
<td>29.07</td>
<td>0.83x10^{-3}</td>
<td>2.01x10^{-6}</td>
</tr>
<tr>
<td>Cl_2(g)</td>
<td>31.72</td>
<td>1.01x10^{-2}</td>
<td>4.04x10^{-6}</td>
</tr>
<tr>
<td>HCl(g)</td>
<td>28.16</td>
<td>1.81x10^{-3}</td>
<td>1.55x10^{-6}</td>
</tr>
</tbody>
</table>

Calculate the heat of formation of \(HCl\) (in
kJ/mole) at standard pressure but 257.5\(^\circ\)C.
and we know all the $C_p's$, so the r.h.s is simple. The l.h.s. is

$$\Delta H(T_{\text{desired}}) - \Delta H(T_{\text{table}}) = \int_{T_{\text{table}}}^{T_{\text{desired}}} \Delta C_p dT$$

3. Calculate the expected adiabatic flame temperature of hydrogen burned in air at 25°C, in which the ratio of hydrogen to air is 1:2 (by moles). Assume

<table>
<thead>
<tr>
<th>Name</th>
<th>$C_p$ Joules/mol°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_p$($H_2$)</td>
<td>29.0</td>
</tr>
<tr>
<td>$C_p$($O_2$)</td>
<td>29.4</td>
</tr>
<tr>
<td>$C_p$($N_2$)</td>
<td>29.1</td>
</tr>
<tr>
<td>$C_p$($H_2O$)</td>
<td>33.6</td>
</tr>
</tbody>
</table>

and $\Delta H^o_f(H_2O(g)) = -242 kJ/mol$. Assume that the actual 'combustion' takes place at 25°C. Assume air is 80% nitrogen and 20% oxygen.

4. Saturated solutions of ammonium chloride are often used in sports to reduce the swelling of a sprained ankle. Calculate the final temperature, if the following reaction

$$\text{NH}_4\text{Cl}(s) + 10\text{H}_2\text{O}(\text{liq}) \rightarrow \text{NH}_4\text{Cl}(\text{aq}, 10\text{H}_2\text{O})$$

takes place starting at 25°C. $\Delta H^o_f(\text{NH}_4\text{Cl}(\text{aq}, 10\text{H}_2\text{O})) = -71.567 \text{ kcal/mol}$ and that of $\text{NH}_4\text{Cl}(s) = -75.15 \text{ kcal/mol}$. The specific heat of the solution is 3.77 kJ/(kg°C).

Answer and/or Hint

$$\frac{-71.567 - (-75.16)}{3.77 \times 0.2335} = \Delta t$$

where the heat of reaction is begin obtained from the athlete's hand, hence the sign. (Only partial units have been used.)

Don't forget to lower the temperature by $\Delta t$ from 25°C.

III. EPILOGUE

After editing this material for weeks, and continuously finding errors, some small, some huge, I have to wrap it up and send this off. If, in the years 2008-2010 or so, you come across an error, and you e-mail me, I will try to have it corrected.

But since this material is written in LaTeX there is some doubt whether or not I’ll have access to a Linux machine, and access to the digitalcommons site. You can try; we’ll see what happens, if anything. Thanks to all the students over the last 45 years who’ve taught me Physical Chemistry.