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

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Problems for the Advanced Physical Chemistry Student
Part 5, 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 problems are being taken from the web and are being edited, their statements and the hints/answers offered are subject to the typical editorial errors that ensue when such work is undertaken in the vacuum of a non-teaching situation. 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 2_{nd} LAW

1. Calculate the expected adiabatic flame temperature of hydrogen burned in a stoichiometric amount of air. Assume $(C_p(O_2)(g)) = 29.35$ J/(mol^{o}K). Assume $(C_p(H_2O(g)) = 33.577$ and ΔH (standard, formation) = -241.814 kJ/mol. Assume $(C_p(N_2(g))$ = 29.12 J/(mol^{o}K). Assume that the actual 'combustion' takes place at 25^{o}C. Assume air is 80% nitrogen and 20% oxygen.

Answer and/or Hint

We're burning H_2 in air, in a perfect (stoichiometric) 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 air, which contains 2 moles N_2 and creates 1 moles of H_2O according to the equation

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

at 25^{o}C.

Therefore, the equation

$$-\Delta H_{combustion} = \int_{273+25}^{273+T_{flame}} \left(2C_p(N_2) + C_p(H_2O)\right) dT$$

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. ΔH_f^o of HCl(g) is -92.31 kJ/mole at 25^{o}C. The heat capacities are given in the form:

$$C_p(T) = A + BT + CT^2$$

where T is in ^{o}K and C_p is in Joules/(mole K).

Name	A	B	C
H_2(g)	29.07	$0.83x10^{-3}$	$2.01x10^{-6}$
Cl_2(g)	31.72	$1.01x10^{-2}$	$4.04x10^{-6}$
HCl(g)	28.16	$1.81x10^{-3}$	$1.55x10^{-6}$

Calculate the heat of formation of HCl (in kJ/mole) at standard pressure but 257.5^{o}C.

Answer and/or Hint

When we need to work at temperatures other than "table" temperatures, and when we need to work at pressures other than "table" pressures, we need to know how to extend "table" values to the new conditions, hence this problem.

We know that

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p$$

so

$$\left(\frac{\partial \Delta H}{\partial T}\right)_p = \Delta C_p$$

which means that

$$\int_{T_{table}}^{T_{desired}} \left(\frac{\partial \Delta H}{\partial T}\right)_p dT = \int_{T_{table}}^{T_{desired}} \Delta C_p dT$$

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and we know all the $C_p's$, so the r.h.s is simple. The l.h.s. is

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

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

Name	$C_p \frac{Joules}{mol^oC}$
$C_p(H_2(g)$	29.0
$C_p(O_2(g)$	29.4
$C_p(N_2(g)$	29.1
$C_p(H_2O(g)$	33.6

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

Answer and/or Hint

This is a fun problem, as are all flame temperature problems, in that we're able to calculate something "useful".

We're burning H_2 in air, in a 1:2 mole ratio. 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 we have 2 moles of air, which contains 8/5 moles N_2 and 2/5 moles of O_2. Therefore the actual stoichiometry we're dealing with is one mole of H_2 versus 2/5 moles of O_2.

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

at 25^{o}C. Clearly, we're lacking in O_2 which means that the exit gas will be a mixture of water vapor, H_2 (left over) and N_2 (carried through from beginning to end, but not involved in the combustion). We need to heat all these effluent gases using the ΔH of combustion of the amount of H_2 actually consumed.

The details are left to the interested student.

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

$$NH_4Cl(s) + 10H_2O(liq) \rightarrow NH_4Cl(aq, 10H_2O)$$

takes place starting at 25^{o}C.
$\Delta H_f^o(NH_4Cl(aq, 10H_2O))$ = -71.567 kcal/mol and that of NH_4Cl(s) = -75.15 kcal/mol. The specific heat of the solution is 3.77 kJ/(kg^{o}K).

Answer and/or Hint

$$-\frac{-71.567 - (-75.16) kcal/mol}{3.77\frac{1.987}{8.314} \times 0.2335\ kg/mol} = \Delta t$$

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

Don't forget to lower the temperature by Δt from 25^{o}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 digitialcommons 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.