MathCAD for Physical Chemistry
The First Law of Thermodynamics

Prerequisites

Know the definition for heat capacity. Heat capacities of each substance are T dependant. You should know how to find data for heat capacities. For instance the following table gives the coef. of the expression \( \text{Cp (JK}^{-1} \text{ mol}^{-1}) = c_1 + c_2 T + c_3 T^2 + c_4 T^{-2} \) [J. Noggle, Physical Chemistry, Harper-Collis, 1996] which is good in the T range 298K<T<2000K.

<table>
<thead>
<tr>
<th>Gases</th>
<th>c1</th>
<th>c2</th>
<th>c3</th>
<th>c4</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>44.58</td>
<td>15.6x10(^{-3})</td>
<td>-2.95x10(^{-6})</td>
<td>-7.97x10(^{5})</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>26.06</td>
<td>17.7x10(^{-3})</td>
<td>-2.63x10(^{-6})</td>
<td>2.20x10(^{5})</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>29.75</td>
<td>25.10x10(^{-3})</td>
<td>---</td>
<td>-1.55x10(^{5})</td>
</tr>
</tbody>
</table>

Definitions:


Read and practice the MathCAD exercises in Chapter 2 of Noggle’s “Physical Chemistry Using MathCAD”. Concentrate on sections 2.1, 2.2, 2.3 and 2.5 Sections 2.4 and 2.6 can be skipped for now.

Things to learn and skills to acquire:

- More on graphs with MathCAD
- MathCAD can evaluate definite integrals. Find the calculus palette and the button for definite integral. Be able to use it to integrate a given function.
- Mathcad can take derivatives of given functions. The calculus palette also has a derivative button. You can define functions with derivatives as part of the definition. E.g., \( \text{ip(V,T):=}T^{*},\text{shift+/>P(V,T)<tab>T<space bar>-P(V,T).} \)
- Interpolation with the spline fit functions and the interp function.
- Exercise with the root function. E.g. type \( x: =2 \) and \( \text{root(ln(x)-1/x,x)=} \); this will give you the value of x that satisfied the transcendental equation \( \ln(x) = 1/x. \)
Problems

1. (a) Calculate the molar heat capacities of CO$_2$, and H$_2$O and NH$_3$ at 25 Celsius.
   (b) Make a graph of the heat capacity in the temperature range 295 K<T<1000K.
   (c) Calculate the enthalpy change for heating one mole of CO$_2$, and H$_2$O and NH$_3$ from 298K to 1500 K at constant P.

2. Work Noggle problem 2.2. Interpolation can be done in several ways. Use MathCAD’s built in *pspline* and *interp* functions (see handout and Mathcad Help, Index, Interp function).
   An alternative approach is to perform a least squares fit of the given data to a model function. (Not suggested here)

3. Work Noggle problem 2.3. Base your solution on the results of #2. For instance, begin with a copy of your solution #2; then add to this a function for $\Delta H (T1, T2)$ when the initial and final temperatures, T1 and T2 are given.

4. Work Noggle problem 2.5. For ethylene (C$_2$H$_4$), using the RK gas law, make a graph of the internal energy imperfection vs. volume at 300K (volume range as in preceding problem). Calculate this quantity for volumes 0.1, 1.0 and 10 liters per mole. (the constant a and b are 0.4526 Pa m$^6$ mole$^{-2}$ K$^{0.5}$ and 57.01 $10^{-6}$ m$^3$ mole$^{-1}$)
   Refer to Noggle page 55. The answers in the book are different than the ones you will get using the given values of a and b).