Assignment on non-equilibrium thermodynamics.

The problems in this assignment need to be solved using a symbolic math program. I provided an example of a kinetics problem in Mathcad that I got from Carey Bissonette. This type of solution will work for this problem set. The help pages in Mathcad can help you sort out what is done. Alternatively use Mathematica. You can follow the Mathematica syntax of the problem as it is solved in Kondepudi. I have not tried these problems myself yet, and you may have to try things out a bit to get it to work. I would be interested to receive the Mathcad or Mathematica solution.

A. Problems from Kondepudi on the non-linear regime.

In the text by Kondepudi (chapter 11) or Kondepudi and Prigogine (Chapter 19) there are some nice Mathematica problems/codes given (see e.g. appendix 11.1 A and 11.1 B). I think it would be instructive to look at these problems and change the parameters, e.g. initial concentrations slightly. The book also contains information when parameters reach their critical value (see K&P ch. 19 for more details). These examples nicely illustrate the general concepts.

I find it a little puzzling why the backward reactions are excluded. I understand it makes the math easier, but after all we can use Mathematica and the like. In principle the codes in the book can be modified to include backward reactions using some reasonable (small) rate constants for the backward reactions. Presumably this would not change the solutions very much (I am not sure, non-linear equations can behave unpredictably. The bifurcation point will likely be affected). If the backward reactions are included, you can calculate the rate of entropy production following the general formula

\[ P = R \sum_{r} (R_{r+} - R_{r-}) \ln(R_{r+} / R_{r-}) \].

According to Prigogine, entropy production is a driving force behind these phenomena. How does this quantity evolve with time? Does it reach some kind of minimum?

B. Exploring chemical reactions using concepts from non-equilibrium thermodynamics and kinetics in the linear regime.

In this assignment I will make an attempt to discuss some of the topics we looked at in class, and try some kinetics simulations. The assignment is based on a single model system, which is fairly complex, and certainly needs to be solved in a symbolic math program. I am not sure if the problem will work well. It is my attempt to try to understand the issues.
Consider a unimolecular system that has 4 stable minima A, B, C, D. The reactions and transition states connecting the various minima for this system are depicted in the figure below.

![Diagram of the unimolecular system with 4 stable minima A, B, C, D and reaction pathways]

In the Table below I provide tentative values for the molar Gibbs free energy for both the stable species (A, B, C, D) and the transition states 1,2,3,4 and 5. I am providing these in units of RT for convenience. They should be declared as variables (or parameters) in your program, such that they can easily be changed.

Table of molar Gibbs free energies:

<table>
<thead>
<tr>
<th>species</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu^0 = E / RT$</td>
<td>10</td>
<td>11</td>
<td>14</td>
<td>15</td>
</tr>
</tbody>
</table>

Table of molar activation energies

<table>
<thead>
<tr>
<th>Transition state</th>
<th>1=AB</th>
<th>2=BC</th>
<th>3=CD</th>
<th>4=AD</th>
<th>5=AC=BD</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu^0 = ETS / RT$</td>
<td>14</td>
<td>22</td>
<td>17</td>
<td>20</td>
<td>30</td>
</tr>
</tbody>
</table>

I chose the barriers, such that A & B and also C & D might easily equilibrate, but it is somewhat harder to reach the C & D products if initially we have only A (high barriers for both reactant A and B). You might raise or lower barriers 1,2 and/or 5 to model (or play with) this feature. Playing around with the barriers might also change what we call elementary reactions. If the barriers are very high we can simply discard a reaction without affecting equilibrium. For example raising barrier 2 also to 30 (as in barrier 5), the species C & D are accessed using only the A-D reaction step.
The Gibbs free energy for each species in units of RT is given in terms of the mole fraction of the species

\[ \mu_a(x_a) = \mu_a^0 + RT \ln x_a \rightarrow \mu_a^0 + \ln x_a \]

The forward and backward rate constants can be calculated from transition state theory (or using Arrhenius law), for example

\[ k_{AB} = \exp(-(E_{TS1} - E_A)) = \exp(-(16 - 10)) = e^{-6}, \]

and

\[ K_{DA} = \exp(-(E_{TS5} - E_D)) = \exp(-(30 - 15)) = e^{-15}, \]

where we take the pre-exponential factor to be the same for each reaction, and set it to unity. This just sets the time-scale.

1. Thermodynamic equilibrium.

Let us first establish the concentration of each species at equilibrium. We have the conditions

\[ G = \sum_a x_a \mu_a = \sum_a x_a \mu_a^0 + x_a \ln x_a \]

\[ \sum_a x_a = 1 \]

Calculate the equilibrium concentration by minimizing the free energy subject to the constraint on the mole fractions, e.g. minimize the function

\[ F = G - \lambda (\sum_a x_a - 1) \]

You should find that

\[ x_a = \frac{e^{-\mu_a^0}}{\sum_a e^{-\mu_a^0}}, \]

similar to the Boltzmann distribution. You might also check that at equilibrium the chemical potential for each isomer is equal. Each isomer could be viewed as a ‘phase’ of the unimolecular species. Different phases are in equilibrium if they have the same chemical potential.

2. Kinetics for reaching thermodynamic equilibrium.

Set up the rate equations (in terms of the mole fractions, assume we have 1 mol in total) for each of the 4 species, and solve the coupled rate equations (using Mathematica as in Kondepudi) to reach the stationary states (in the long time limit). In the initial conditions you might start with excess D or excess A. To do part 3 of this question, you have to make sure none of the initial concentrations are 0. You might check the following:

a. The same stationary state is reached independent of the starting conditions: thermodynamic equilibrium. It may take a long time though.

b. The same stationary state is reached independent of the rate constants (e.g. you might change the parameters ETS1 through ETS5), in particular lowering ETS5 such that it is lower than ETS2 or ETS4 may lead to much faster rate towards equilibrium.

c. At equilibrium the forward and backward rates for each reaction are equal (detailed balance).
3. Rate of Entropy production.

Calculate the rate of entropy production as you reach equilibrium. You can calculate the sum 
\[ P = \sum_{r} (R_{r+} - R_{r-}) \ln \left( \frac{R_{r+}}{R_{r-}} \right) \], and monitor each term in the sum (entropy production in individual reactions). All of them are positive and they reach (more or less) zero at different times, (I think). Every time a term hits zero, you have reached thermal equilibrium for that particular reaction. I think that once a term in the entropy production has reached zero it will not move away from it. This would relate to the discussion in Kondepudi about equilibrium in different subsystems.


At the stationary solution one can calculate the first and second derivatives of the entropy production \( P \) with respect to the concentrations. The first derivatives will be zero, and the matrix of second derivatives will be a positive definite symmetric matrix

\[ P^{\text{eq}} = \frac{1}{2} \sum_{i,j} \frac{\partial^2 P}{\partial x_i \partial x_j} \delta x_i \delta x_j \rightarrow \sum_{j} F_j \delta x_j . \]

This would seem a good way to define Onsager forces, Onsager ‘flows’ and Onsager coefficients. The matrix is necessarily positive definite since \( P \) reaches a minimum. It is also obviously symmetric. These results are almost trivial and I think it is due to the definition of the flows. I am myself still a bit puzzled about the manipulations that were necessary at various parts of the discussion to derive the Onsager coefficients and to establish their symmetry and positive definiteness. Here it seems trivial, using the above definitions of ‘flow’.

5. Exploring kinetics while keeping some concentrations fixed: non-equilibrium thermodynamics.

Take the concentrations of A and D to be fixed at certain stationary values \( A_0 \) and \( D_0 \) (try to find something reasonable, e.g. a smallish change from the thermodynamic stationary state). Then use the rate equations for the species B and C to calculate the stationary state solutions in which

\[ \frac{d[B]}{dt} = \frac{d[C]}{dt} = 0 . \]

You can check that (or if) the stationary states are stable by starting from slightly different initial concentrations, and solving the differential rate equations to obtain the stationary states in the long time limit. For this case you should see that the concentrations in the stationary state do depend on the given concentrations \( A_0 \) and \( D_0 \), and on the rate constants. You can change these variables to check this behaviour. Since the rate equations are linear I do not anticipate instabilities or multiple stationary states. This would mean that no matter what you choose for the initial concentrations of B and C you should reach the same solution.

I am not sure about the mass balance in these equations. By simply setting

\[ \frac{d[B]}{dt} = \frac{d[C]}{dt} = 0 \]

we will find stationary concentrations for B and C. If we then substitute all these values in the rates for A and D (equations we do not use to get the B and C
concentrations) we find the values for \( \frac{d[A]}{dt}, \frac{d[D]}{dt} \) in the stationary state. I think the interpretation should be that these are the flows of A and D to be provided, such that while reacting the concentration of A and D stay at their stationary values A0 and D0, at least in the stationary state. This indicates that this kind of experiment is not so trivial. One tries to keep the concentrations of A and D constant and adjusts the flows until this works.

6. Examining the rate of entropy production for this case (A=A0, D=D0). We can use the same formula for the rate of entropy production as before, and see how it evolves as a function of time. It will reach a point at which the entropy production stays constant. Using Mathematica/Mathcad you can take the derivative of the entropy production \( \frac{\partial P}{\partial [C]}, \frac{\partial P}{\partial [B]} \) at the stationary point. In my understanding of Kondepudi & Prigogine the claim is that this quantity would have reached a minimum. In the analysis I did (on paper), it is not necessarily true that the entropy production is stationary at the stationary state concentrations of B and C. I think it would be interesting to check this. I suspect that the proper procedure would be to minimize entropy production under a suitable constraint, e.g. that the total number of moles of C+B is constant at their stationary value. Hence you might try to optimize \( F(n_B, n_C) = P - \hat{\lambda}(n_B + n_C - n_{0+B+C}) \), adding all 6 reactions in P. Or one might need to optimize P under the constraint that \( \frac{d[A]}{dt}, \frac{d[D]}{dt} \) have the appropriate stationary state values. I am not sure about any of this. Perhaps stationarity of P is reached at the appropriate stationary values of all quantities. It would be a very nice result if a suitable (understandable) formula for the rate of entropy production could be found that would lead to the same stationary state concentrations calculated using stationary state kinetics. I do not know how it can be done, and have not seen this issue addressed in the literature.

7. Onsager relations anyone? They were related to the rate of entropy production in the linear regime. Do we know the formula for P?

These are some of the questions that you might investigate. It is quite possible that the issues can be resolved while experimenting on the computer. This is part of scientific investigation. In my experience computer simulations often greatly help to understand a formalism, and help to phrase to proper questions. I am interested to pursue this further and look forward to your work.