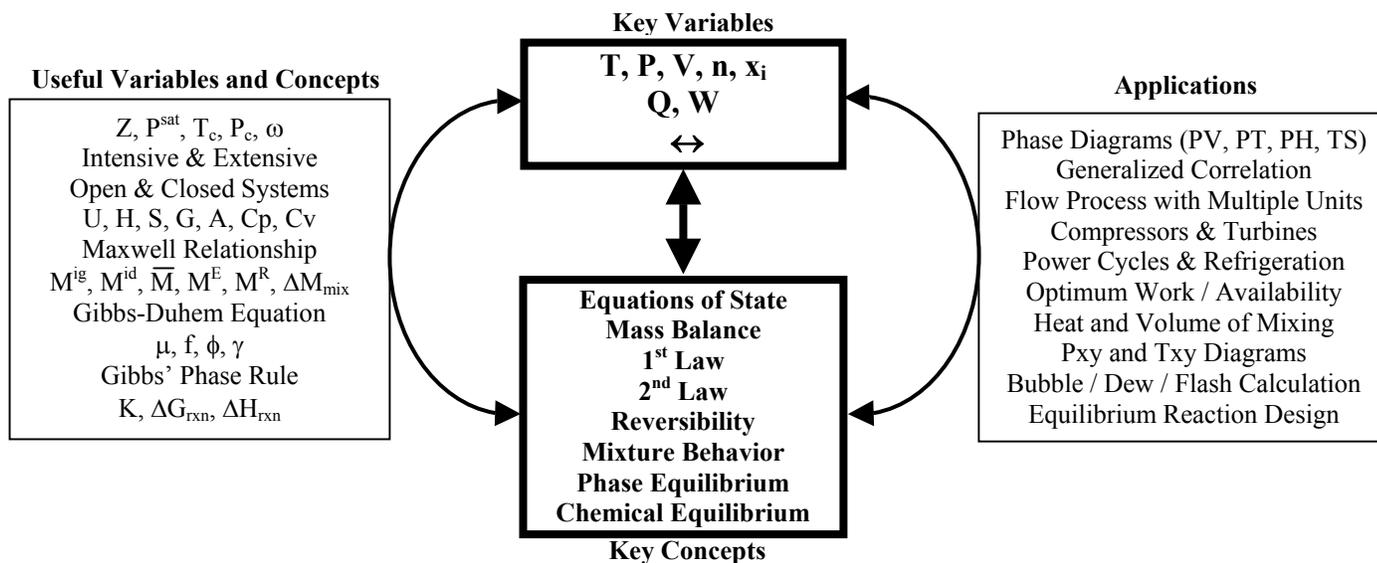


We are now at the end of our long, bumpy, and tortuous 10.213 journey. I invite you to look back at the road we've been through and see what we have learned. What's the point of doing Thermo? How is this going to affect me? What's the big picture? These are the questions I hope to address. People have different ways of viewing Thermo, but this is the way I see it.



The main things we are concerned with I have labeled “**Key Variables.**” These are *real* variables, measurable in a more or less straightforward way: temperature, pressure, volume, amount (mass/moles), composition in mixture, heat, and work. The arrow \leftrightarrow represents another important question: “where do we end up: react more to left or right? liquid, vapor, both?” etc.

To answer these questions, people formulated the “**Key Concepts**” based on empirical observation and practical needs. For example, mass balance and the laws of Thermodynamics come from observation of the real world. Equations of state (EOS) were initially formulated for the very practical need to relate T, P, and V; later on, as we saw, the EOS is also useful in calculating Q and W.

In the development of “Key Concepts” through the history of Thermo, other variables proved useful. These variables do *not* have a real physical existence. However, they're easier to deal with because they enable *concise mathematical forms* of the “Key Concepts”. These are the “**Useful Variables and Concepts**”. They exist for a very practical purpose, not merely to give Thermo students a hard time!

An example follows. Enthalpy is a *made-up* variable; after all there is no enthalpymeter. It becomes very useful, however, in the energy balance of an open system: $\Delta(mH) = Q + W_s$. The end goal is to relate flow rate, heat, and work (Key Variables) via 1st Law (Key Concept).

Besides learning to deal with the “Key Variables”, we also learned some real-world application of these concepts. Some of these are listed under “**Applications**”. They are ultimately also concerned with T, P, n, x, Q, etc. However, they are problems commonly encountered in Chemical Engineering and it's useful to learn how to write and solve them efficiently.

What have we *not* learned? In addition to more rigorous and specialized topics in Thermo itself, there are other aspects of Chemical Engineering that we have avoided completely. Perhaps the most important is the question, “*How do things get there?*” We have been interested mostly in the equilibrium, the endpoint. The process is not the main concern. We cannot tell from Thermo how long it takes to reach equilibrium. For these, we need fluid mechanics, mass and heat transfer, and reaction kinetics (in 10.301, 10.302 and 10.37).

Cheesy speech follows... A bigger question: How is Thermo going to affect your life (other than what it already did to your sleeping pattern)? Well, this one is up to you. Thermo is real; it's there and it works! There is Thermodynamics in most things we do and there are implications that may not be obvious at first.

Having said all that, the most important thing to get out of this class, in my opinion, is to feel *empowered* by this tool you learned. Later on, you may need to blow the dust and crack open your textbook and lecture notes because you don't remember the formulae. You should be aware, however, that there are ways in which T, P, W, Q, n, and equilibrium are related. Yes, it's a crazy world out there, but there are some order and rules in it. And like it or not ... you've come to know more of them than before.

A general approach to problems

This approach probably takes too much time in the exam; get used to thinking this way before the exam. But if you're really stuck in the exam, go through this check list. When reviewing / doing practice problems, think about the following:

Setting Up

- 1) What is the system that I am choosing? The whole process, one equipment, part of an equipment?
- 2) Do I need to break up the problems into several parts (e.g. for a power cycle)?
- 3) What is it that I want to find out? What information is given in the problem?

Identifying Components

- 4) Is my system open or closed?
- 5) If there is a gas, is it ideal? If there is a solution, is it ideal?
- 6) How many species participates in the process? Is there a mixture somewhere?
- 7) Are there more than one phase in the process? Are they in contact and in equilibrium?
- 8) Is there a reaction in the process? Is it in equilibrium?
- 9) What are the changes that are happening? W , Q , W_s ? Is P constant? Is T constant? Is V^t constant? Is V constant? Is it adiabatic? $\Delta H = 0$? $\Delta S = 0$?

Check List

- 10) Is an **equation of state** going to tell me something useful? Ideal gas, vdW, generalized correlation?
- 11) Do I need to write **material balance** on the system?
- 12) Is **1st Law** useful?
- 13) Is **2nd Law** relevant?
- 14) If I have a **mixture**, I have to treat it differently from a pure system.
- 15) If there is **phase equilibrium**, I can use phase equilibrium equation (such as Raoult's law, whichever is appropriate).
- 16) If there is **reaction equilibrium**, I can use reaction equilibrium equation ($K = \exp(-\Delta G^\circ/RT) = \Pi \dots$ etc)

Familiar Things

- 17) Have I seen this **unit operation** before? Turbine, compressor, pump, heat exchanger? Power cycle, refrigeration? A mixing tank? A flash tank?
- 18) Have I seen this type of calculation before? Getting γ from G^E/RT , dew point, bubble point, azeotrope?

Calculating Thermodynamic Variables

- 19) How do I get P , T , V , H , G , U and S (whatever is applicable) for a **pure system**?
 - a) Am I dealing with an ideal gas? There should be expressions for these in the notes (prepare them).
 - b) If it's a real gas, are there data at the back of the book (steam, tetrafluoroethane, etc)?
 - c) If it's real and there are no data, am I given an equation of state to use (vdW, Redlich Kwong, etc)?
 - d) If it's real, there are no data, and no EOS is specified, then I must use generalized correlation. How do I calculate P , T , or V , or ΔH and ΔS for this?
- 20) How do I get P , T , V , H , G , U and S (whatever is applicable) for a **mixture**?
 - e) Is it an ideal solution? There should be expressions for these in the notes (prepare them).
 - f) If it's not an ideal solution, are there data in the book (Hx diagram for H_2SO_4 , etc.)?
 - g) If it's real and there are no data, am I given a deviation from ideal to use? e.g. M^R , M^E

Of course, there are some special problems that cannot be solved this way (e.g. Problem 17 in Pset E) and require some thinking outside this scheme.

1)

In an ammonia production process, 1 mol/s of N_2 and 3 mol/s H_2 are fed into a reactor at $25^\circ C$ and some pressure P_{reactor} . The reaction proceeds to equilibrium. The stream of product and unreacted reactants is then fed into a flash separation tank operating at $-50^\circ C$ and 1 bar, where a liquid stream and a vapor stream are produced. The liquid stream, 0.1 mol/s flow rate, is essentially pure NH_3 .

The vapor stream from this flash tank is fed into another flash tank operating at a different temperature and pressure, producing yet another pair of vapor and liquid streams: the vapor rich in H_2 ($y_{H_2} = 0.99$) and the liquid rich in N_2 ($y_{N_2} = 0.98$). There is no NH_3 in these two streams.

Assuming that gases are ideal and solutions are also ideal, calculate:

- The pressure of the reactor,
- The amount of heat produced/required by the reactor if the stream comes out at $25^\circ C$.

2) (adapted from Final Exam Fall 1999)

Consider a power cycle having four steps:

Step I: Saturated vapor at 300 K and 4 bar is reversibly condensed at constant pressure to form saturated liquid. In this step heat, Q_- , is removed from each kg of the working fluid and work (boundary and shaft) is neither required nor produced.

Step II: Isentropic compression to supercritical fluid at a pressure of 40 bar. This requires 100 kJ of work to be performed on each kg of the working fluid.

Step III: Heat, Q_+ , is added to each kg of the working fluid. The pressure remains constant while the temperature increases to 600 K. Work (boundary and shaft) is neither required nor produced.

Step IV: Isentropic expansion during which 500 kJ of work is produced by each kg of the working fluid.

For the working fluid:

- the critical point occurs at 450 K and 30 bar.
 - the enthalpy of vaporization at 300 K is 1500 kJ/kg
 - the heat capacity of the supercritical fluid at 600 K is 4 kJ/kg K
- Draw a TS diagram showing all four steps in the power cycle. Include the vapor-liquid dome.
 - Calculate Q_-
 - Calculate Q_+
 - What is the efficiency of the cycle?

3)

In yet another spectacular derring-do, A reacts into B ($A \leftrightarrow B$) in the liquid phase.

This reaction happens in a vessel where both vapor and liquid exist; both A and B are present in both phases. However, the reaction only occurs in the liquid phase. This occurs at 300 K where $P_A^{\text{sat}} = 0.5$ atm, $P_B^{\text{sat}} = 1$ atm, and $\Delta G^\circ_{\text{rxn}} = 1728$ J/mol. The liquid interaction is well described by $G^E/RT = Cx_Ax_B$.

Initially 2 moles of A are placed in the vessel; after equilibrium is reached, the liquid was found to be 10 mol% A. Using the information above, determine:

- The value of C
- The composition of the vapor.
- The pressure of the vessel.
- The amount (moles) of the two phases, if a total of 1 mole of A is in the vessel.

4)

An adiabatic reversible compressor is used to compress 1 mole/s of air (20% O₂ and 80% N₂) from ambient condition to 2 atm. For the process condition, $S^R = RT_{O_2}y_{N_2}/(300\text{ K})$ and $H^R = RT_{O_2}y_{N_2}$. You can assume that C_p of both O₂ and N₂ are constant = 2.5R.

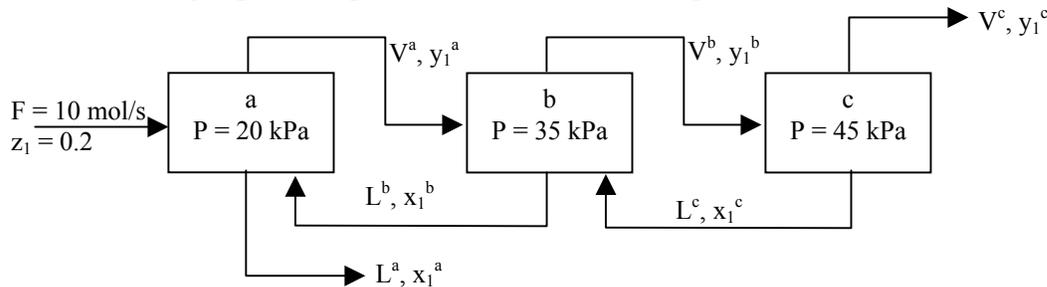
- Setup the calculation for the final temperature.
- Calculate the work required. Use 386 K for value of final temperature.

5) (adapted from Final Exam Fall 1998)

An inventor claims to have created a fuel-cell device that produces 115 kW of electricity using the reaction of H₂ and O₂ to form steam. The schematic of the device given to you shows that the device uses 1 mole/s of air (20% O₂ and 80% N₂) and stoichiometric amount of H₂ as feed. The H₂ and air come in as separate streams, both at 100 kPa. Apparently, the O₂ and H₂ react with 100% conversion in the device. The product stream is also at 100 kPa. No claim is made about whether the device is adiabatic or not but the inventor insists that all operation is to be carried out at room temperature (298 K). Is this device possible? You can assume that the gases are ideal.

6)

Consider the following separation process where the boxes represent flash tanks:



The system is methanol (1) and 1-propanol (2). The whole process is at 50°C. The Pxy diagram at this temperature is given on the next page. Determine V^c (mol/s) and y₁^c (mole fraction of 1 in vapor c). The following information can be used:

- The solution behavior can be approximated by the model: $G^E = RT(0.8x_1 + 0.5x_2)x_1x_2$
- The vapor can be considered ideal.

7) (adapted from Final Exam Fall 1997)

CO and H₂ are used to produce methanol CH₃OH in an all-gas process as follows:

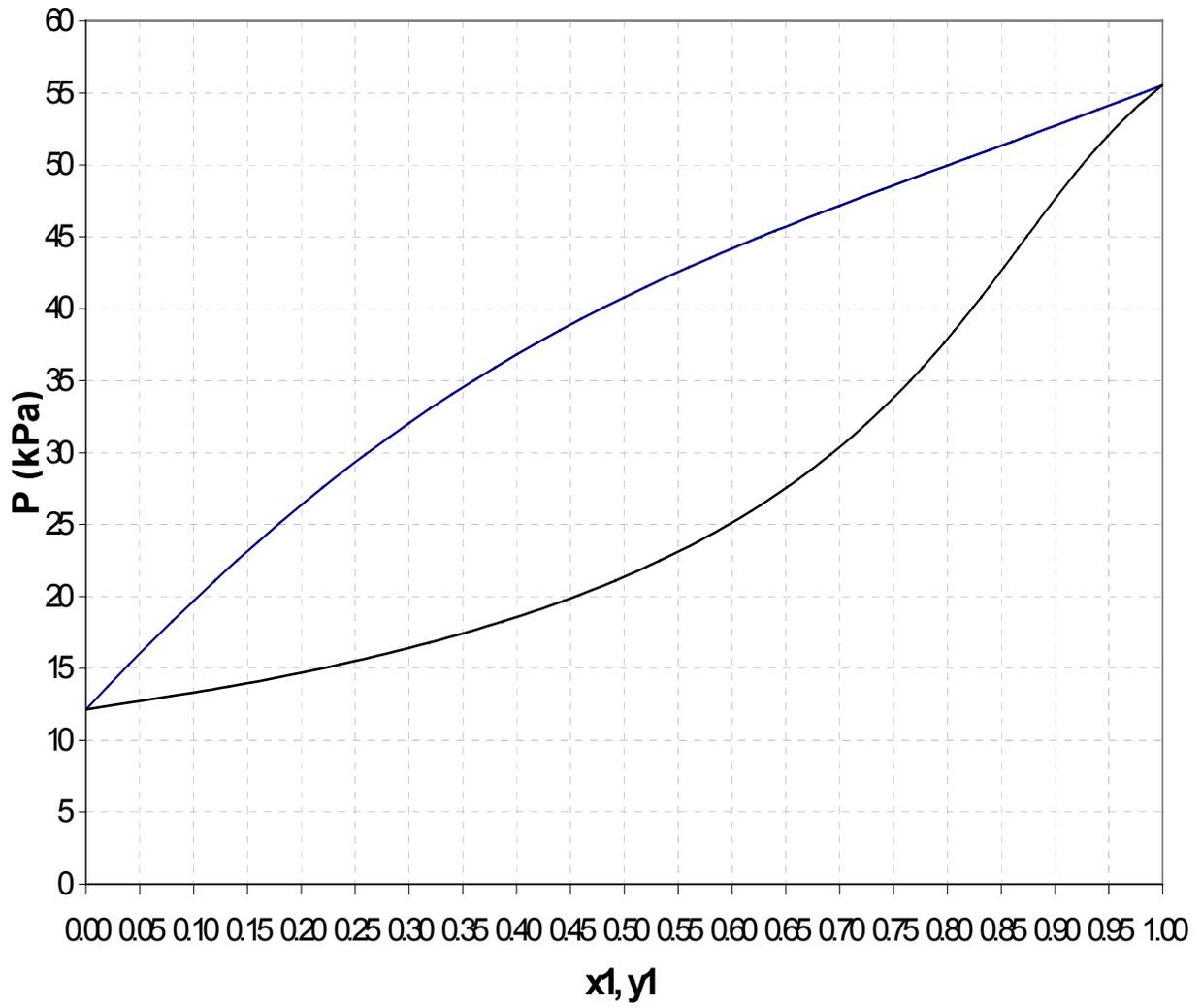
- Pure H₂ and CO are mixed with a recycle stream (described below). This mixture is then fed into a reactor operating at 500 K and 15 bar.
- The outlet of the reactor contains the product and unreacted reactants. This stream enters a separation vessel, which produces two streams. One stream is pure methanol, while the other contains CO and H₂. The latter is recycled into the reactor (after mixing with pure H₂ and CO as described above).

Calculate the total flow rates of the recycle stream if 10 mol/s of CH₃OH is produced. (If computation of final number is too difficult, just set it up such that there is only one unknown).

The following can be assumed:

- The reaction in the reactor reaches equilibrium.
- The C_p 's are approximately constant at these values: CO = 1.5R, H₂ = 1.5 R, CH₃OH = 4.5R.
- In general, the gases are not ideal but form ideal solution. Only H₂ can be assumed to be ideal.

Pxy diagram for methanol and 1-propanol at 50°C



More difficult (?) variations on the problems

Problem 1:

- Calculate the extra heat required if we want to heat up the stream coming out of the reactor to 50°C .
- Is it okay to assume ideal gas? Assuming the gases to be non-ideal (but form ideal solution), set up the problem to solve for pressure of the reactor.

Problem 2:

- Instead of being given the enthalpy of vaporization, you are told that the entropy of vaporization at 300 K is 5 kJ/kg K . Redo the problem.
- Compare the efficiency of the engine to that of Carnot engine with the same T_{high} and T_{low} .

Problem 3: The reaction is in the gas phase, not in the liquid phase. Redo the problem

Problem 4:

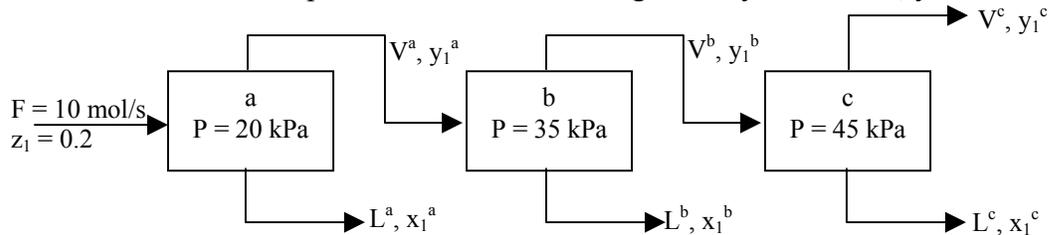
- The inlet is not one stream of air, but two separate streams: 0.2 mol/s of O_2 and 0.8 mol/s of N_2 , both at ambient condition. Redo the problem.
- Everything is the same, except that the compressor is 80% efficient. Redo the problem.

Problem 5:

- What is the maximum work that can be produced by the device?
- The reactor outlet pressure is not 100 kPa but 8 kPa. Redo the problem.

Problem 6:

Let's deconstruct the distillation process. Instead of having the recycle streams, you have something like this:



Determine all the compositions in all the streams and the molar amount of each stream.

Problem 7:

Consider that this problem does not exist. Give yourself a little break.
Good luck on the exam!