1. Chemical Thermodynamics
   a) solution: breaking solute/solute; solvent/solvent; forming solute/solvent interactions in stepwise or concerted mechanism
   b) chemical reactions: reactants connected on a potential energy surface to products thermodynamics: subject of initial and final states kinetics: reaction path/activation barriers
   c) Can we predict what goes and when?
   d) What do we have to start with? Tabulated
      \( \Delta H^\circ \) enthalpy, heat of reaction
      \( \Delta G^\circ \) free energy, maximum amount of work
      \( S^\circ \) entropy, probability of disorder/order
   e) Examples:
      combustion of methane (model reaction for burning fuel in your car)
      \[
      \text{CH}_4(g) + 2 \text{O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{H}_2\text{O}(l)
      \]
      at 1 atm, 25 ºC from Appendix Four in your textbook
      \[ \Delta H_{\text{rxn}} = -890 \text{ kJ}, \Delta G_{\text{rxn}} = -818 \text{ kJ}, \Delta S^\circ = -243 \text{ J/K} \rightarrow \text{what do these mean} \]

2. Entropy:
   • increased probability of mixing
   • measure of molecular disorder/randomness
   • nature spontaneously proceeds toward states/conditions that have the highest probability of existence
   • gas in containers: \( A(n) \) connected to \( B(0) \) ⇒ wait ⇒ \( A(N/2) + B(N/2) \) if \( A = B \) (pV=nRT of not!)
     positional probability: finding all molecules in \( A = (\frac{1}{2})^n \)
   • liquid in container: smaller volumes → less positions available (\( S_{\text{liquid}} << S_{\text{gas}} \)); but mix two liquids together and thus increase the possibilities of microstates (\( S_{\text{liquid}} ++ \))
   • solid in container: similar condensed volume – similar or less positions (\( S_{\text{solid}} < S_{\text{liquid}} \))

3. Spontaneity:
   • spontaneous process → capable of doing work ⇒ from above definition \( \Delta G < 0 \)
   • non-spontaneous process → need to do work to make the process occur ⇒ \( \Delta G > 0 \)
   • equilibrium process → reversible process takes place ⇒ \( \Delta G = 0 \); \( \Delta H = T \Delta S \)
   • in a spontaneous process there is always an increase in the entropy (\( \Delta S > 0 \)) – resulting in a disordered state
   • What is increasing specifically? \( \Delta S_{\text{Universe}} = \Delta S_{\text{System}} + \Delta S_{\text{Environment}} \)
   • 2\textsuperscript{nd} law of thermodynamics: \( \Delta S_{\text{Universe}} > 0; \Delta S_{\text{System}} + \Delta S_{\text{Environment}} > 0 \rightarrow \text{compare and contrast to 1\textsuperscript{st} law} \)
   • 3\textsuperscript{rd} law of thermodynamics: for a completely ordered pure crystalline solid the \( S \) at 0 K is zero

4. Determination of Entropy:
   Start at an equilibrium situation: \( T = 100 \text{ ºC} \) (environment temperature is at the boiling point)
   • no work is gained or need to be put in; entropy is directly related to enthalpy/heat
   • \( \text{H}_2\text{O}(l) \leftrightarrow \text{H}_2\text{O}(g) \rightarrow \text{evaporation} \Delta H_{\text{vap}} = 44.0 \text{ kJ/mol} \Rightarrow \Delta S = \Delta H_{\text{vap}} / T; \) (118 J/mole K)
   • heat is taken away from surroundings (endothermic) – molecules in the environment slow down, get less disordered. \( \Delta S_{\text{System}} = -\Delta S_{\text{Environment}} \Rightarrow \Delta S_{\text{Universe}} = 0 \) ⇒ characteristic of an equilibrium process
   Non-equilibrium: \( T = 110 \text{ ºC} \) (raise environment temperature above boiling point)
   • \( \Delta S_{\text{System}} = \Delta H_{\text{vap}} / 373 \text{ K} + m \ c_p (110-100) \text{ ºC} / 383 \text{ K} \)
   • \( \Delta S_{\text{Environment}} = -\Delta H_{\text{vap}} + m \ c_p (110-100) \text{ ºC} / 383 \text{ K} \)
   • \( \Delta S_{\text{Universe}} = \Delta H_{\text{vap}} / 373 - \Delta H_{\text{vap}} / 383 > 0 \) – spontaneous process, it will take place and can be used for useful work
   • entropy change is determined by heat flow