Relaxation in Glass: Review of Thermodynamics

Lecture 9: Thermodynamic Concepts and the Law of Thermodynamics

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Definitions

- System – That part of the universe set aside for special study
- Boundary – The region of space that defines the system
- Surroundings – All parts of the universe except the system
- Isolated system – A system that does not exchange energy or matter with the surroundings
- Closed system – A system that may not exchange matter with the surroundings, but may exchange energy
- Open system – A system that may exchange matter and energy with its surrounding
- Homogenous system – A system that consists of one phase and may be considered as uniform throughout
- Heterogeneous system – A system that consists of more than one phase and may be consider as not being uniform throughout

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Some more definitions…

- Phase(s) – A part of a system that has unique defined thermodynamic properties that characterizes itself from other possible parts of the system
- Component – A unique chemical element, compound, or material that has unique chemical and thermodynamic properties
- Solution – A homogeneous system consisting of more than one component
- Mixture – A heterogenous system consisting of more than one component
- State – The thermodynamic condition of the system
- State variable – A thermodynamic property that depends only upon the properties of the thermodynamic state of the system
- State function – A thermodynamic property that may depend upon other thermodynamic properties and whose value only depends upon the thermodynamic state of the system
- Intensive variables (properties) – Properties of the system that are independent of the size of the system
- Extensive variable (properties) – Properties of the system that are dependent upon the size of the system

Some more definitions…

- Process – A series of one or more changes in the properties of a system
- Transformation – A process that (typically) changes the phase of a system
- Transition – Typically synonymous with transformation, but commonly refers to changes between equilibrium phases
- Equilibrium – A condition of a system that is described by the appropriate thermodynamic function to be a global minimum (or maximum) of the thermodynamic function
- Equilibrium state – A state of a system that is described by the appropriate thermodynamic function to be a global minimum (or maximum) of the thermodynamic function
- Non-equilibrium state – A state of a system that is not described by the appropriate thermodynamic function to be a global minimum (or maximum) of the thermodynamic function

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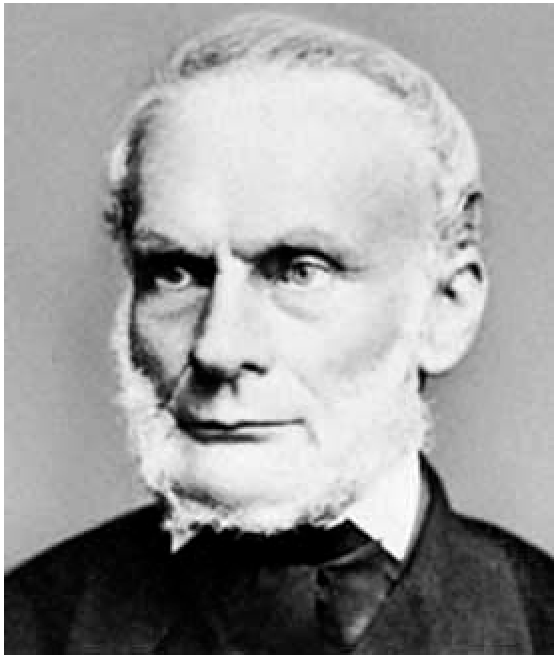
A few more definitions…

- Metastable state - A state of a system that is described by the appropriate thermodynamic function to be a local minimum (or maximum) of the thermodynamic function
- Ergodic states – Those states of a system that are considered as equilibrium states of the system that the system has explored to arrive at the final equilibrium state of the system
- Non-ergodic states – Those states of a system that are not considered as equilibrium states of the system and the system has been restricted to because it has had insufficient time to explore all of the ergodic states of the system
- Energy – Is thermodynamic capacity to do work
- Conservation of Energy – In all processes, energy can be transformed from one kind to another, but it can neither be created nor destroyed
- Work – Is the quantity of energy transferred in a system due to external changes in the surroundings of a system

1st Law of Thermodynamics

“Die Energie der Welt is ein Konstant”

Rudolf Julius Emanuel Clausius 1822-1888



“the best you can do is to break even…”

http://en.wikipedia.org/wiki/Rudolf_Clausius

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1st Law of Thermodynamics

- Mathematical formulation…for the universe

$$\sum dU = \sum \delta q + \sum \delta w = 0$$

- An alternative expression…for a system

$$dU = \delta q - \delta w - \delta w_{other}$$

- An alternative expression… for a system

$$\Delta E = q - w$$

1^{st} Law of Thermodynamics

- Now, let’s consider the heat changes: Note all reversible processes

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_V$$

$$dU = C_V dT$$

$$dU = \delta q - p_{ext} dV$$

$$dU = C_V dT - p_{ext} dV$$

$$U \equiv U(T,V)$$

- The “natural” variables of U are T, V

1^{st} Law of Thermodynamics

- Consider temperature and pressure conditions, much more commonly observed and used

$$dU = \delta q - p_{ext} dV$$

- Consider the definition of the function:

$$H \equiv U + PV$$

$$dH = dU + pdV + VdP$$

$$dH = \delta q + VdP$$

$$dH = C_p dT + VdP$$

$$H \equiv H(T, P)$$

- The natural variables of H are T,P and are the common laboratory variables

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The Enthalpy function:

- The natural variables of H are T and P

$$H \equiv H(T,P)$$

$$dH = C_P dT + VdP$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P(T,P)$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V(T,P)$$

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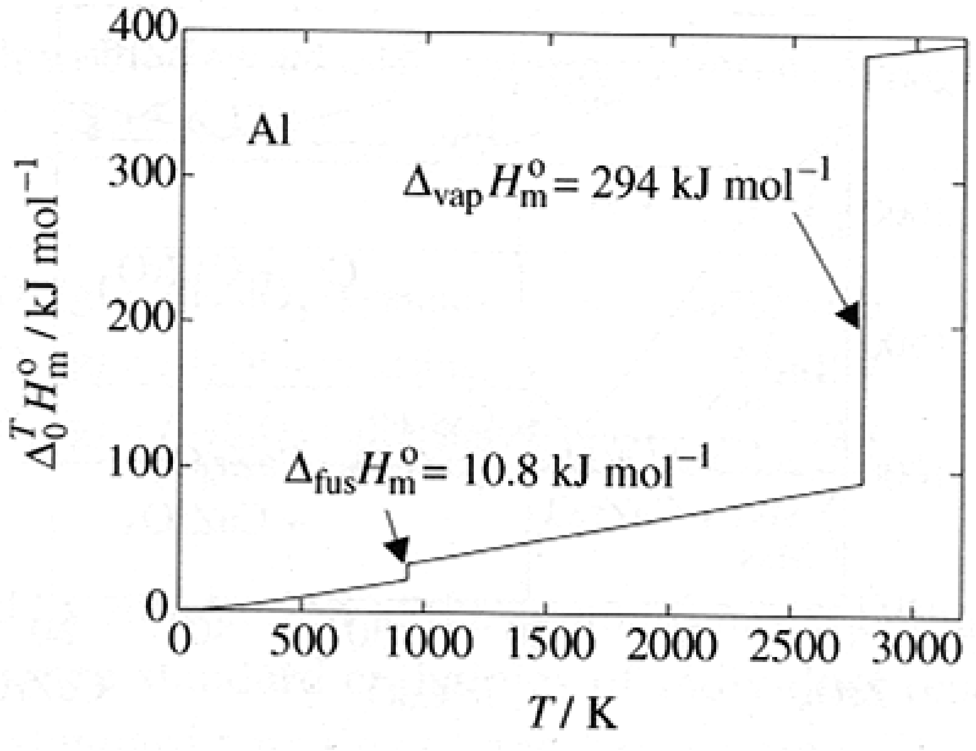
Enthalpy function and heat capacities

- Typical values…



Standard enthalpy of Al relative to 0 K.

Multi-Variable Calculus of Thermodynamic Functions

- We need to consider that thermodynamic functions are multi-variable functions
- Consider the volume function….

$$V(T,P,n)$$

$$dV_{P,n} = \left(\frac{\partial V}{\partial T}\right)_{P,n} dT$$

$$dV_{T,n} = \left(\frac{\partial V}{\partial P}\right)_{T,n} dP$$

$$dV_{P,T} = \left(\frac{\partial V}{\partial n}\right)_{T,P} dn$$

$$dV(T,P,n) = \left(\frac{\partial V}{\partial T}\right)_{P,n} dT + \left(\frac{\partial V}{\partial P}\right)_{T,n} dP + \left(\frac{\partial V}{\partial n}\right)_{T,P} dn$$

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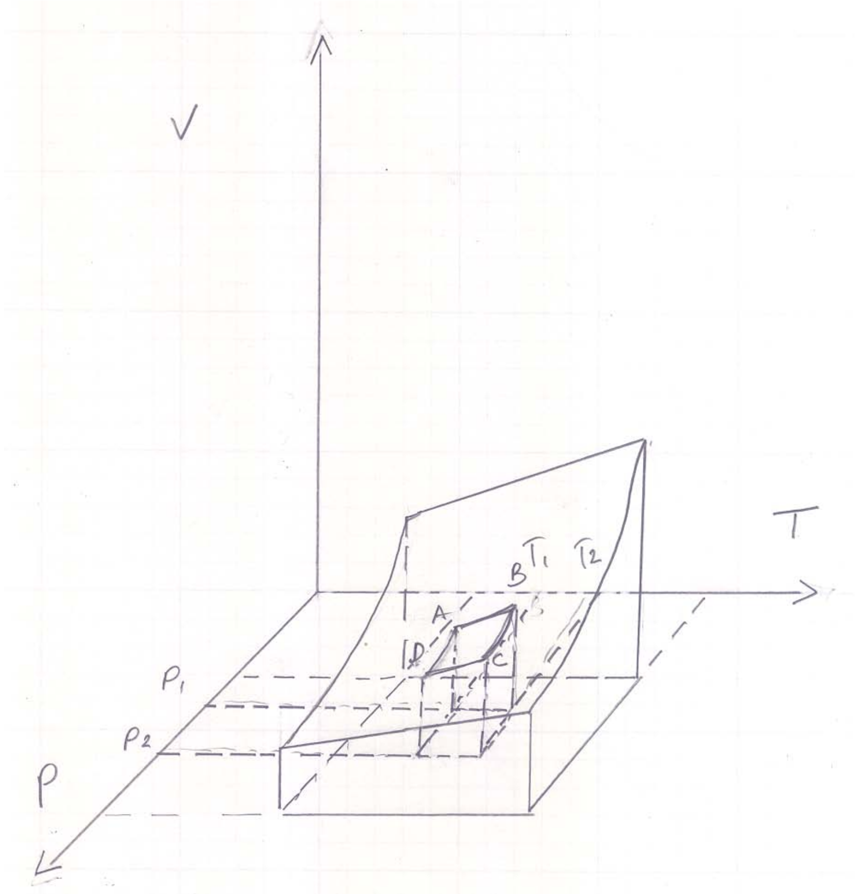
Multi-Variable Calculus of Thermodynamic Functions

- Consider the 3-d V(T, P) surface (constant n)



Multi-Variable Calculus of Thermodynamic Functions

- Exercise… apply this to the ideal gas…PV=nRT

$$V(T,P,n)$$

$$dV_{P,n} =$$

$$dV_{T,n} =$$

$$dV_{P,T} =$$

$$dV(T,P,n) =$$

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Multi-Variable Calculus of Thermodynamic Functions

- Now consider finite changes in state of the system:

$$\Delta V \equiv V_2(T_2,P_2,n_2)-V_1(T_1,P_1,n_1)$$

$$\int_{V_1}^{V_2} dV_{P,n} = \Delta V_{P,n} =$$

$$\int_{V_1}^{V_2} dV_{T,n} = \Delta V_{T,n} =$$

$$\int_{V_1}^{V_2} dV_{P,T} = \Delta V_{P,T} =$$

- Exercise…1 mole, 298 K, 1 atm → 10.8 moles, 997K, 0.143 atm

Multi-Variable Calculus of Thermodynamic Functions

Consider constant volume processes, dV = 0

$$dV(T,P,n) = \left(\frac{\partial V}{\partial T}\right)_{P,n} dT + \left(\frac{\partial V}{\partial P}\right)_{T,n} dP + \left(\frac{\partial V}{\partial n}\right)_{T,P} dn \equiv 0$$

$$V = \frac{nRT}{P} \equiv C$$

$$\left(\frac{\partial V}{\partial T}\right)_{P,n} dT + \left(\frac{\partial V}{\partial P}\right)_{T,n} \left(\frac{\partial P}{\partial T}\right)_{V,n} dT \equiv 0$$

$$P(T) = \frac{nRT}{C}$$

$$\left(\frac{\partial V}{\partial T}\right)_{P,n} + \left(\frac{\partial V}{\partial P}\right)_{T,n} \left(\frac{\partial P}{\partial T}\right)_{V,n} \equiv 0$$

$$dP = \left(\frac{\partial P}{\partial T}\right)_{V,n} dT$$

$$\left(\frac{\partial P}{\partial T}\right)_{V,n} = -\left(\frac{\partial V}{\partial T}\right)_{P,n} \Big/ \left(\frac{\partial V}{\partial P}\right)_{T,n}$$

$$dP = \frac{nR}{C} dT$$

Multi-Variable Calculus of Thermodynamic Functions

- We could have started with T instead of P

$$V = \frac{nRT}{P} \equiv C$$

$$T(P) = \frac{PC}{nR}$$

$$dT = \left(\frac{\partial T}{\partial P}\right)_{V,n} dP$$

$$dT = \frac{C}{nR} dP$$

$$\left(\frac{\partial V}{\partial T}\right)_{P,n} \left(\frac{\partial T}{\partial P}\right)_{V,n} dP + \left(\frac{\partial V}{\partial P}\right)_{T,n} dP \equiv 0$$

$$\left(\frac{\partial V}{\partial T}\right)_{P,n} \left(\frac{\partial T}{\partial P}\right)_{V,n} + \left(\frac{\partial V}{\partial P}\right)_{T,n} \equiv 0$$

$$\left(\frac{\partial T}{\partial P}\right)_{V,n} = -\left(\frac{\partial V}{\partial P}\right)_{T,n} \Bigg/ \left(\frac{\partial V}{\partial T}\right)_{P,n}$$

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Multi-Variable Calculus of Thermodynamic Functions

- Reciprocity Theorem:

$$\left(\frac{\partial T}{\partial P}\right)_{V,n} = 1\Big/\left(\frac{\partial P}{\partial T}\right)_{V,n} \quad \text{Or} \quad \left(\frac{\partial V}{\partial T}\right)_{P,n} = 1\Big/\left(\frac{\partial T}{\partial V}\right)_{P,n}$$

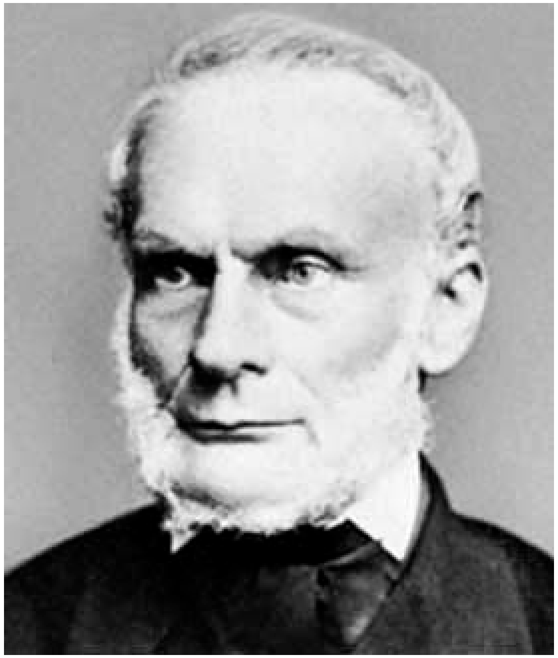
- Exercise….Check with the ideal gas law
- Exercise….Apply to the van der Waals equation of real gases what is : $\left(\frac{\partial V}{\partial T}\right)_{P,n}$

$$\left[P+\frac{a^2n^2}{V^2}\right]\left[V-nb\right]=nRT$$

2nd Law of Thermodynamics

"Die Entropie der Welt strebt einem maximum zu"

Rudolf Julius Emanuel Clausius 1822-1888



"the best you can do is to break even, and…. you can't even do that…"

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2nd Law of Thermodynamics

- Universal postulate of science:

  "A system left to is own in a given circumstance, will behave in one and only one manner and only through the application of an external force, is it possible to alter this direction of change, the direction to the final equilibrium state of the system"

- Even for an isolated system, enormous changes can take place, $\Delta E = 0$, the 1st law of thermodynamics is an insufficient metric of process direction
- Degradation of energy is in itself insufficient
- A new function is needed, needs to be invented, to help determine the final equilibrium state of the system
- Entropy has been found to be a helpful function…

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2^{nd} Law of Thermodynamics – reversible processes

- Consider the very simple system:
  - A mass m falls (reversibly) a distance h through a viscous medium generating an amount of heat q = mgh
  - Or a heating wire run for a fixed time $q = P \cdot t = I^2R\ t$
  - This system is then connected thermally to a reservoir of temperature T_H and the heat flows spontaneously into the reservoir
  - We could also have connected the system to a colder reservoir, T_L , and allowed the heat to flow into the colder reservoir
  - Our instinct tells us that the second process is more spontaneous that the second, indeed if $T_H = T_R$ then no heat would have moved between system and surroundings
  - This can be shown by placing the hot reservoir between the system and colder reservoir and the same amount of heat would travel between the system to the hot reservoir and then to the cold reservoir

2^{nd} Law of Thermodynamics – reversible processes

- A simple function that has this property is:

  $\Delta S = q_{rev}/T,$

  where T is the temperature of the system receiving the heat flow q
- $\Delta S_H = q_{rev}/T_H < \Delta S_C = q_{rev}/T_C$
- $\Delta S_C = \Delta S_{res} + \Delta S_H$

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2^{nd} Law of Thermodynamics – reversible processes

- Now for infinitesimal changes $dS = \delta q_{rev}/T$
- Consider the reversible heating of a material,
  - $T_{system} = T_{surr} + \delta T$, *where* δT *is a small infinitesimal value*
  - *Constant pressure heating*

$$dS_i = \frac{\delta q_{i,rev}}{T_i}$$

$$\Delta S(T_1 \to T_2) = \int_{T_1}^{T_2} dS = \sum_{T_1}^{T_2} \frac{\delta q_{i,rev}}{T_i} = \sum_{T_1}^{T_2} \frac{dH_i}{T_i} = \int_{T_1}^{T_2} \frac{C_P(T)}{T} dT$$

  - *Constant volume heating*

$$dS_i = \frac{\delta q_{i,rev}}{T_i}$$

$$\Delta S(T_1 \to T_2) = \int_{T_1}^{T_2} dS = \sum_{T_1}^{T_2} \frac{\delta q_{i,rev}}{T_i} = \sum_{T_1}^{T_2} \frac{dU_i}{T_i} = \int_{T_1}^{T_2} \frac{C_V(T)}{T} dT$$

2nd Law of Thermodynamics – reversible processes

- For isothermal reversible processes at constant volume:

$$\int dS = \Delta S = \int \frac{\delta q_{rev}}{T} = \frac{\Delta U(T)}{T}$$

- For isothermal reversible processes at constant pressure:

$$\int dS = \Delta S = \int \frac{\delta q_{rev}}{T} = \frac{\Delta H(T)}{T}$$

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2nd Law of Thermodynamics – irreversible processes

- Now considering the process of heating a material where the system and surroundings are not at the same temperature, that is there is a finite heating rate driven by a finite temperature
- In this case there will be irreversible processes that are driven by the non-equilibrium heat flows between the system and surroundings

$$dS = \frac{\delta q_{irr}}{T} + dS_{irr}$$

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2nd Law of Thermodynamics – irreversible processes

- There will be irreversible heat flows and irreversible entropy changes:

$$dS = \frac{\delta q_{irr}}{T} + dS_{irr}$$

- Now since the entropy function is a state function, in order to calculate the entropy changes easily from the heat flows we must "invent" a reversible path to connect the initial and final states and determine the ***reversible*** heat flows that would be associated with that now ***reversible*** process

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2nd Law of Thermodynamics – irreversible processes

$$dS = \frac{\delta q_{irr}}{T} + dS_{irr} = \frac{\delta q_{rev}}{T}$$

- In our heating example, the system goes from temperature T_1 to temperature T_2, the system change is independent of how the temperature was changed
- Consider perhaps the simplest heating, our system is heated from T_1 to T_2 by a surrounding at T_2

$$dS_i = \frac{\delta q_{i,rev}}{T_i}$$

$$\Delta S(T_1 \rightarrow T_2) = \int_{T_1}^{T_2} dS = \sum_{T_1}^{T_2} \frac{\delta q_{i,rev}}{T_i} = \sum_{T_1}^{T_2} \frac{dH_i}{T_i} = \int_{T_1}^{T_2} \frac{C_P(T)}{T} dT$$

2^{nd} Law of Thermodynamics – irreversible processes

- Now the surroundings however, did not have a change in temperature:

$$\Delta S_{surr} = q_{surr}/T_{surr} = q_{surr}/T_2$$

- Consider the two processes:
- Reversible (equilibrium) heating of ice from -25 C to 0 C, melted at 0 C and then reversibly warmed to 25 C
- Irreversible (non-equilibrium) melting of ice from -25C to water at 25 C
- Exercise: What is ΔS_{H2O}, ΔS_{surr} *and* ΔS_{univ} for each process?
- Take Cp(ice) = 2.1J/g-^{o}C, Cp(water) = 4.2J/g-^{o}C, $\Delta H_{melting}$ = 333.6 J/g

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2nd Law of Thermodynamics – irreversible processes

- For irreversible processes, the entropy change in the system is still the same so long as the system changes between the two same initial and final states, the entropy is a state function
- However, the entropy change in the universe is now non-zero, we do more than exchange disorder between the system and surroundings, we create more disorder in the universe in the irreversible processes

$$dS \geq \frac{\delta q}{T}$$

$$\Delta S_{univ}^{irr} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

2^{nd} Law of Thermodynamics – irreversible processes

- The challenge is to "invent" a reversible process that connects the initial and final states of our system along a reversible path (entropy is a state function)
- And do the same for the surroundings…
- In each case, entropy is a state function, and can be more easily determined through the reversible heat, the question becomes, what is the reversible heat for the irreversible process?

2nd Law of Thermodynamics – Direction towards equilibrium

- Consider an isolated system…

$$dS \geq \frac{\delta q}{T} = \frac{\delta q_{rev}}{T}$$

$$dS_{isolated} = 0 \quad \delta q = 0$$

- The entropy increases as irreversible processes take place, and then at equilibrium, the entropy ceases to change and has arrived at a maximum

"Die Entropie der Welt strebt einem maximum zu"

- So, for an isolated system, the entropy function increases toward a maximum

2^{nd} Law of Thermodynamics – Direction towards equilibrium

- So for an isolated system, the entropy can be used to tell the direction of spontaneous change, the direction that increases the entropy of the system
- The challenge of course is to do science on isolated systems, we need a function that operates under conditions that are more common
- Constant T and P?
- Constant T and V?
- Let's see if we can "invent" a function that will give us the same ability to predict the position of equilibrium, but for a system that is contained under more commonly used conditions

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