Midterm Notes/Review

Lecture 2 03/29 (wed)

First Law
- $dE = đQ - đW$ ← Always true

Second Law
- $\Delta S \geq 0$
- Clausius's statement:
  "Heat cannot by itself pass from a colder to a hotter body."
  - $\Delta S = -đQ/T_A + đQ/T_B = đ\left[1/T_B - 1/T_A\right] < 0$
- Kelvin's statement:
  "A process whose only effect is the complete conversion of heat into work cannot occur."

Third Law
- As $T \to 0_+$, $S \to S_0 = 0$

Review of Math in Thermodynamics

- $$\frac{d}{dx}\left(f(x)+g(x)\right)=\frac{d}{dx}f(x)+\frac{d}{dx}g(x)$$

- **Product Rule:**

$$\frac{d}{dx}\left(f(x)g(x)\right)=f(x)\frac{d}{dx}\left[g(x)\right]+g(x)\frac{d}{dx}\left[f(x)\right]$$

OR $$\frac{d}{dx}\left(\frac{f(x)}{g(x)}\right)=\frac{g(x)\frac{d}{dx}\left[f(x)\right]-f(x)\frac{d}{dx}\left[g(x)\right]}{g(x)^2}$$

- **Chain Rule:**

$$\frac{df}{dx}=\frac{df}{du}\cdot\frac{du}{dx}$$

- $$\left(\frac{\partial}{\partial y}\right)_x\left(\frac{\partial f}{\partial x}\right)_y=\frac{\partial^2 f}{\partial y\partial x}$$

Automatic

Can be combined in this way.

$$=$$

$$\left(\frac{\partial}{\partial x}\right)_y\left(\frac{\partial f}{\partial y}\right)_x=\frac{\partial^2 f}{\partial x\partial y}$$

Order makes no difference

- <u>Reciprocal Rule</u>:

$$\left(\frac{\partial y}{\partial x}\right)_f \text{ and } \left(\frac{\partial x}{\partial y}\right)_f \longrightarrow f(x,y)=0$$

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = 0$$

$$\left(\frac{\partial f}{\partial x}\right)_y dx = -\left(\frac{\partial f}{\partial y}\right)_x dy$$

$$\Rightarrow \left(\frac{\partial x}{\partial y}\right)_f = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_f} \leftarrow \text{Reciprocal Rule}$$

- <u>Cyclic Rule</u>:

$$f(x,y,z)=0 \longrightarrow \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial y}{\partial z}\right)_x = -1$$

Can be rearranged at will.

Lecture 3 04/02 (Fri)

Simple Applications of Macroscopic Thermo

- $p = \dfrac{nRT}{V - nb} - a\dfrac{n^2}{V^2}$

- Isothermal Compressibility K_T

  $$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

- Isobaric Volumetric thermal expansion

  $$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \quad , \quad p = p(V,T)$$

- Properties of Ideal Gas
  - Equation of State $PV = nRT$
  - Energy $E(T) = (\partial E/\partial V)_T = 0$

  ⊛ $dE = dE(T,V) = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV$

  ⊛ $T\,dS = dE + p\,dV$

Ex. Relate S, T, V with 1 equation

$$TdS = dE + pdV \Rightarrow dS = \frac{1}{T}dE + \frac{p}{T}dV$$

Plugging in dE, we get

$$dS = \frac{1}{T}\left[\left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV\right] + \frac{p}{T}dV$$

$$= \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_V dT + \left[\frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T + \frac{p}{T}\right]dV$$

we are given that $S = S(E,V)$, so

$$dS = \left(\frac{\partial S}{\partial E}\right)_V dE + \left(\frac{\partial S}{\partial V}\right)_E dV$$

which makes

Important!

$$\boxed{\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V \quad \text{and} \quad \frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_E}$$

and we can say

$$\left[\frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T + \frac{P}{T}\right] \rightarrow \left(\frac{\partial S}{\partial V}\right)_T$$

And,

$$\left(\frac{\partial S}{\cancel{\partial E}}\right)_V \left(\frac{\cancel{\partial E}}{\partial T}\right)_V \rightarrow \left(\frac{\partial S}{\partial T}\right)_V$$

Thus

$$\boxed{dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV}$$

Lecture 4 04/05 (Mon)

Specific Heat

- C_v is molar specific heat at constant volume
  - $C_v = \frac{1}{n}\left(\frac{dE}{dT}\right)_v = \frac{1}{n} C_v$
  - ⊛ $dE = n C_v dT$
- C_p is molar specific heat at constant pressure.
  - $C_p = C_v + R$

Adiabatic Expansion

- An ideal gas that undergoes adiabatic expansion/compression has an equation of state

$$PV^{\gamma} = \text{constant}$$

Lecture 5 04/07 (wed)

Entropy of an ideal Gas

$$S(T, V_0, n) = nC_v \ln(T) + nR\ln(V) + nS_0(T_0, V_0)$$

Lecture 6 04/09 (Fri)

Independent variables S and V

$$TdS = dE + PdV$$

Then, $dE = TdS - PdV \longrightarrow E = E(S, V)$

which is related with

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV$$

meaning that

$$T = \left(\frac{\partial E}{\partial S}\right)_V \quad , \quad -P = \left(\frac{\partial E}{\partial V}\right)_S$$

If we divide these expressions by dV and dS, we get

$$T\left(\frac{\partial}{\partial V}\right) = \left(\frac{\partial E}{\partial S}\right)_V \left(\frac{\partial}{\partial V}\right) \rightarrow \left(\frac{\partial T}{\partial V}\right)_S = \frac{\partial^2 E}{\partial S \partial V}$$

$$-P\left(\frac{\partial}{\partial s}\right) = \left(\frac{\partial E}{\partial V}\right)_s \left(\frac{\partial}{\partial s}\right) \rightarrow -\left(\frac{\partial P}{\partial s}\right)_V = \frac{\partial^2 E}{\partial V \partial s}$$

Making $\boxed{\left(\frac{\partial T}{\partial V}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_V}$ maxwell Relation

Independent Variables S and P

$$dE = Tds - PdV$$

$$= Tds - PdV - VdP + VdP$$

$$= Tds - d(PV) + VdP$$

$$\underbrace{d(E+PV)} = Tds + VdP$$

Enthalpy $H = d(E+PV)$

Meaning that $H = H(s,P)$, and like before we can write

$$dH = \left(\frac{\partial H}{\partial s}\right)_P ds + \left(\frac{\partial H}{\partial P}\right)_s dP$$

$$T = \left(\frac{\partial H}{\partial S}\right)_P \quad , \quad V = \left(\frac{\partial H}{\partial P}\right)_S$$

$$T\left(\frac{\partial}{\partial P}\right) = \left(\frac{\partial H}{\partial S}\right)_P\left(\frac{\partial}{\partial P}\right) \rightarrow \left(\frac{\partial T}{\partial P}\right)_S = \frac{\partial^2 H}{\partial S \partial P}$$

$$V\left(\frac{\partial}{\partial S}\right) = \left(\frac{\partial H}{\partial P}\right)_S\left(\frac{\partial}{\partial S}\right) \rightarrow \left(\frac{\partial V}{\partial S}\right)_P = \frac{\partial^2 H}{\partial P \partial S}$$

Thus, we can say these two terms are equivelant

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P}$$ Maxwell Relation

Independent Variables T and V

using Helmholtz, $E - TS = F$
we get the maxwell relation

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T}$$ Maxwell Relation

Independent variables T and P

using Gibbs Free Energy,

$$G = E + PV$$

we get the relation

$$\boxed{\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P}$$

Maxwell Relation

Lecture 7 04/12(Mon)

Heat capacity at constant V

$$C_V = \left(\frac{đQ}{dT}\right)_V = \left(\frac{T\,ds}{dT}\right)_V = T\left(\frac{ds}{dT}\right)_V$$

Volume = const.

and, $$C_V = \left(\frac{dE + P\,dV}{dT}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V$$

Heat capacity at constant pressure

- $C_P = \left(\frac{đQ}{dT}\right)_P = T\left(\frac{\partial s}{\partial T}\right)_P$
- $\boxed{C_P - C_V = VT\frac{\alpha^2}{k}}$ ← works for both constant P and V
  - where $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$
  - where $k = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ Isothermal compressibility

For an ideal gas, $C_P - C_V = nR$.

Lecture 8 04/14 (Wed)

Entropy and Energy

- $\Delta S = S(T,V) - S(T_0, V_0)$

$$dS(T,V) = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$= \left(\frac{1}{T}\right) \cdot T \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$= \left[\frac{1}{T} \cdot C_V\right] dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$= \frac{1}{T} \cdot C_V(T,V)\, dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

we need these two

To solve for $C_V(T,V)$, we can find it using $C_V(T,V_0)$ and the equation of state.

$$\left(\frac{\partial C_v}{\partial V}\right)_T = \left(\frac{\partial}{\partial V}\right)_T C_v = \left(\frac{\partial}{\partial V}\right)_T \left[T\left(\frac{\partial S}{\partial T}\right)_V\right]$$

$$\Rightarrow \left(\frac{\partial C_v}{\partial V}\right)_T = T\left(\frac{\partial}{\partial V}\right)_T\left(\frac{\partial S}{\partial T}\right)_V$$

$$= T\left(\frac{\partial}{\partial V}\right)_T\left(\frac{\partial}{\partial T}\right)_V \cdot (S)$$

$$= T\left(\frac{\partial}{\partial T}\right)_V\left(\frac{\partial S}{\partial V}\right)_T$$

Now we plug in maxwell eq'n

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\Rightarrow \left(\frac{\partial C_v}{\partial V}\right)_T = T\cdot\left(\frac{\partial}{\partial T}\right)_V \cdot \left[\left(\frac{\partial P}{\partial T}\right)_V\right]$$

$$= T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$ ← 2nd derivative of Pressure

Then we can say

$$C_v(T,V) - C_v(T,V_0) = \int_{T_0}^{T} \left(\frac{\partial C_v}{\partial V}\right)_T dT$$

$$= \int_{V_0}^{V} T \left(\frac{\partial^2 P}{\partial T^2}\right)_{V'} dV'$$

$$\Delta S(T,V) = S(T,V) - S(T,V_0)$$

$$= [S(T,V) - S(T,V_0)] + [S(T,V_0) - S(T_0,V_0)]$$

$$\boxed{\Delta S(T,V) = \left[\int_{V_0}^{V} \left(\frac{\partial P(T,V')}{\partial T}\right)_V dV'\right] + \left[\int_{T_0}^{T} \frac{C_v(T',V_0)}{T'} dT'\right]}$$

Lecture 9 04/16 (Fri)

I don't know or understand what he is doing or why he's doing it. Therefore, I can't write notes on it.