Relaxation in Glass: Review of Thermodynamics

Lecture 10: Thermodynamic Functions

2^{nd} Law of Thermodynamics – irreversible processes

- Exercise for Homework:
- 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-°C, Cp(water) = 4.2J/g-°C, $\Delta H_{melting}$ = 333.6 J/g

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Exercise for Homework:

- Reversible process: $T_{system} = T_{surroundings}$

$$\Delta S_{H_2O} = \int_{248.15K}^{273.15K} \frac{Cp_{ice}}{T} dT + \frac{q_{melt}}{273.15K} + \int_{273.15K}^{298.15K} \frac{Cp_{water}}{T} dT$$

$$\Delta S_{surroundings} = -\int_{248.15K}^{273.15K} \frac{Cp_{ice}}{T} dT - \frac{q_{melt}}{273.15K} - \int_{273.15K}^{298.15K} \frac{Cp_{water}}{T} dT$$

$$\Delta S_{universe} = \Delta S_{H_2O} + \Delta S_{surroundings} = 0$$

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Exercise for Homework:

- Irreversible process: $T_{system} = T_{surroundings}$

$$\Delta S_{H_2O} = \int_{248.15K}^{273.15K} \frac{Cp_{ice}}{T} dT + \frac{q_{melt}}{273.15K} + \int_{273.15K}^{298.15K} \frac{Cp_{water}}{T} dT$$

$$\Delta S_{surroundings} = \frac{-q_{ice}}{T_{surroundings}} = -\left[\int_{248.15K}^{273.15K} Cp_{ice} dT + q_{melt} + \int_{273.15K}^{298.15K} Cp_{water} dT \right]$$

$$\Delta S_{universe} = \Delta S_{H_2O} + \Delta S_{surroundings} \neq 0 > 0$$

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2^{nd} 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

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

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

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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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2nd Law of Thermodynamics – Direction towards equilibrium

- Consider processes at constant T and Volume:

$$dU = \delta q - PdV$$
$$\delta q = dU + PdV$$
$$TdS \geq \delta q$$
$$TdS \geq dU + PdV$$
$$-(dU + PdV) + TdS \geq 0$$
$$consider \quad dT \equiv 0$$
$$d(TS)_T = TdS + SdT = TdS$$
$$-d(U - TS) + PdV \geq 0$$
$$consider \quad dV \equiv 0$$
$$-d(U - TS) \geq 0$$
$$d(U - TS) \leq 0$$

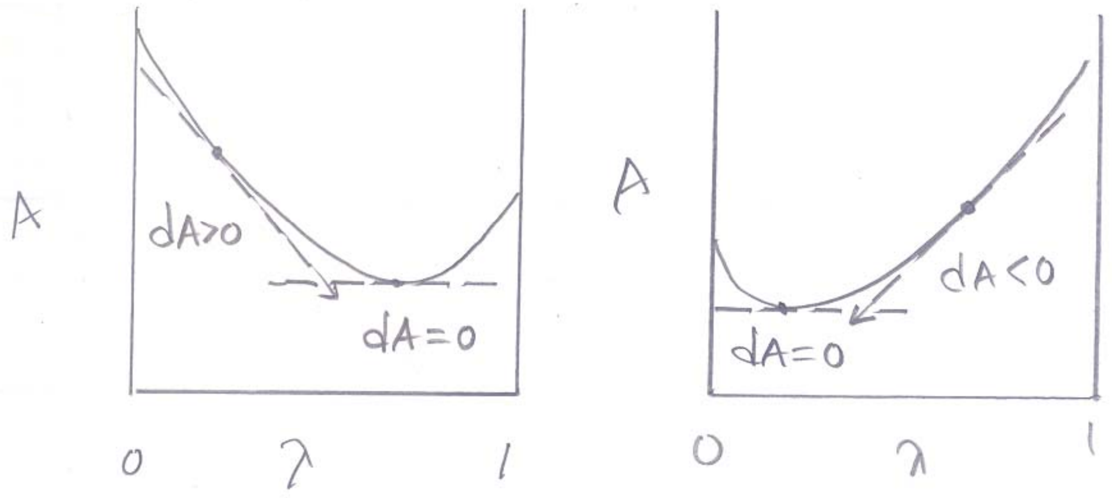
$$U - TS \equiv A$$
$$dA_{T,V} \leq 0$$

The Helmholtz Function decreases for spontaneous processes until it reaches a minimum where after at equilibrium is is unchanged for processes taking place at dT=dP =0

Hermann Ludwig Ferdinand von Helmholtz *(August 31, 1821–September 8, 1894) was a German physician and physicist http://en.wikipedia.org/wiki/Hermann_von_Helmholtz*

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

- So the Helmholtz Function, A(T,V), starts out high and decreases towards equilibrium…



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

- Consider processes at constant Temperature and Pressure

$$dU = \delta q - PdV$$

$$\delta q = dU + PdV$$

$$TdS \geq \delta q$$

$$TdS \geq dU + PdV$$

$$-(dU + PdV) + TdS \geq 0$$

$$consider \quad dP \equiv 0$$

$$d(PV) = PdV + VdP$$

$$-d(U + PV) + TdS \geq 0$$

$$recall \quad H \equiv U + PV$$

$$-dH + TdS \geq 0$$

$$consider \quad dT \equiv 0$$

$$d(TS)_T = TdS + SdT = TdS$$

$$d(H - TS) \leq 0$$

$$H - TS \equiv G$$

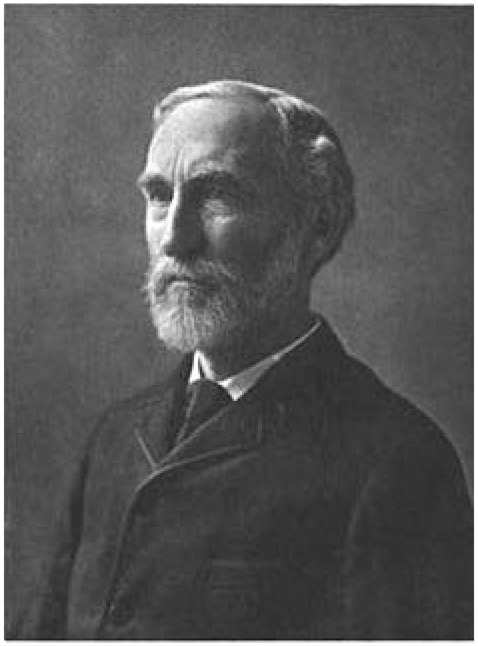
$$dG_{T,P} \leq 0$$

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

- So the Gibbs function decreases for spontaneous processes and reaches a minimum at equilibrium for processes taking place at constant T and P, dT = dP = 0

$$H - TS \equiv G$$

$$dG_{T,P} \leq 0$$



Josiah Willard Gibbs *(February 11, 1839 – April 28, 1903) was an American theoretical physicist, chemist, and mathematician. He devised much of the theoretical foundation for chemical thermodynamics as well as physical chemistry*

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

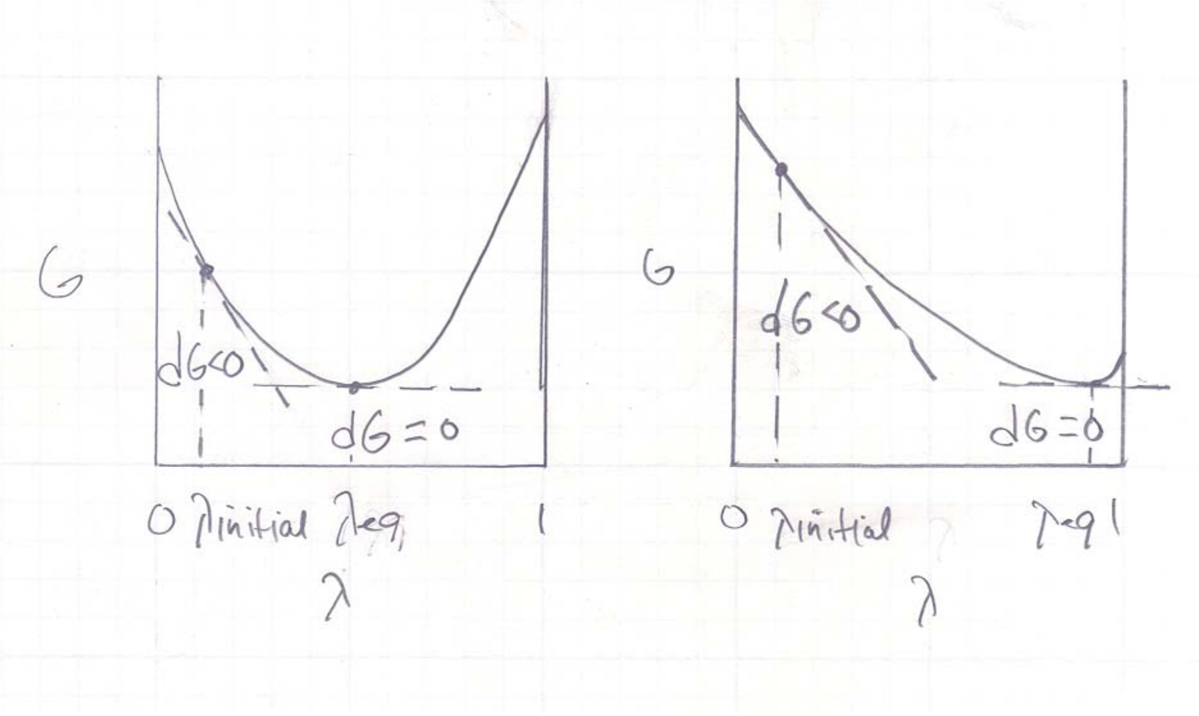
2^{nd} Law of Thermodynamics – Direction towards equilibrium

- So the Gibbs function decreases for spontaneous processes and reaches a minimum at equilibrium for processes taking place at constant T and

  P, dT = dP = 0

$$H - TS \equiv G$$

$$dG_{T,P} \leq 0$$



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2^{nd} Law of Thermodynamics – Thermodynamic Functions

- Our thermodynamic functions so far…

$$U \equiv q - w$$

$$H \equiv U + PV$$

$$A \equiv U - TS$$

$$G \equiv H - TS$$

- Their derivative forms…

$$dU = \delta q - \delta w = TdS - PdV$$

$$dH = TdS - PdV + PdV + VdP = TdS + VdP$$

$$dA = TdS - PdV - SdT - TdS = -SdT - PdV$$

$$dG = TdS + VdP - SdT - TdS = -SdT + VdP$$

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2nd Law of Thermodynamics – Thermodynamic Functions

- Their “natural” variables:

$$U \equiv U(S,V) \qquad dU \equiv \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$H \equiv H(S,P) \qquad dH \equiv \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

$$A \equiv A(T,V) \qquad dA \equiv \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV$$

$$G \equiv G(T,P) \qquad dG \equiv \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

- Exercise: What are the 8 gradients of these functions? For example…

$$\left(\frac{\partial U}{\partial S}\right)_V = ?$$

Thermodynamic Functions… 1^{st} Derivatives

- The first derivative functions

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

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

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

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

Some are more useful than others…

Thermodynamic Functions… 1st Derivatives

- Consider the Gibb's Free-Energy Function…

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

- For a solid phase…

$$\left(\frac{\partial G^s}{\partial T}\right)_P = -S^s \qquad \left(\frac{\partial G^s}{\partial P}\right)_T = V^s$$

- For a liquid phase…

$$\left(\frac{\partial G^l}{\partial T}\right)_P = -S^l \qquad \left(\frac{\partial G^l}{\partial P}\right)_T = V^l$$

- For a gas phase…

$$\left(\frac{\partial G^g}{\partial T}\right)_P = -S^g \qquad \left(\frac{\partial G^g}{\partial P}\right)_T = V^g$$

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Thermodynamic Functions… 1st Derivatives

- Consider the Gibb's Free-Energy Function

$$dG_P = \left(\frac{\partial G}{\partial T}\right)_P dT$$

$$dG_P = -SdT$$

$$\int_{S_1}^{S_2} dG_P = G_2 - G_1 \equiv G(T_2) - G(T_1) = \int_{T_1}^{T_2} -S(T)dT$$

Thermodynamic Functions… 1st Derivatives

- $S^s(T) < S^l(T) < S^g(T)$

$$\left(\frac{\partial G^s}{\partial T}\right)_P = -S^s < \left(\frac{\partial G^l}{\partial T}\right)_P = -S^l < \left(\frac{\partial G^g}{\partial T}\right)_P = -S^g$$

$$\bar{S}^{o,s}(T,P) = \bar{S}^o(0,P) + \int_0^{T<Tm} \frac{Cp^s(T)}{T} dT$$

$$\bar{S}^{o,l}(T,P) = \bar{S}^o(0,P) + \int_0^{Tm} \frac{\bar{Cp}^s(T)}{T} dT + \Delta \bar{S}^o_{melt} + \int_{Tm}^{T<Tb} \frac{\bar{Cp}^l(T)}{T} dT$$

$$\bar{S}^{o,v}(T,P) = \bar{S}^o(0,P) + \int_0^{Tm} \frac{\bar{Cp}^s(T)}{T} dT + \Delta \bar{S}^o_{melt} + \int_{Tm}^{Tb} \frac{\bar{Cp}^l(T)}{T} dT + \Delta \bar{S}^o_{vap} + \int_{Tb}^{T} \frac{\bar{Cp}^g(T)}{T} dT$$

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Thermodynamic Functions… 1^{st} Derivatives

- Temperature Dependence of the Entropy

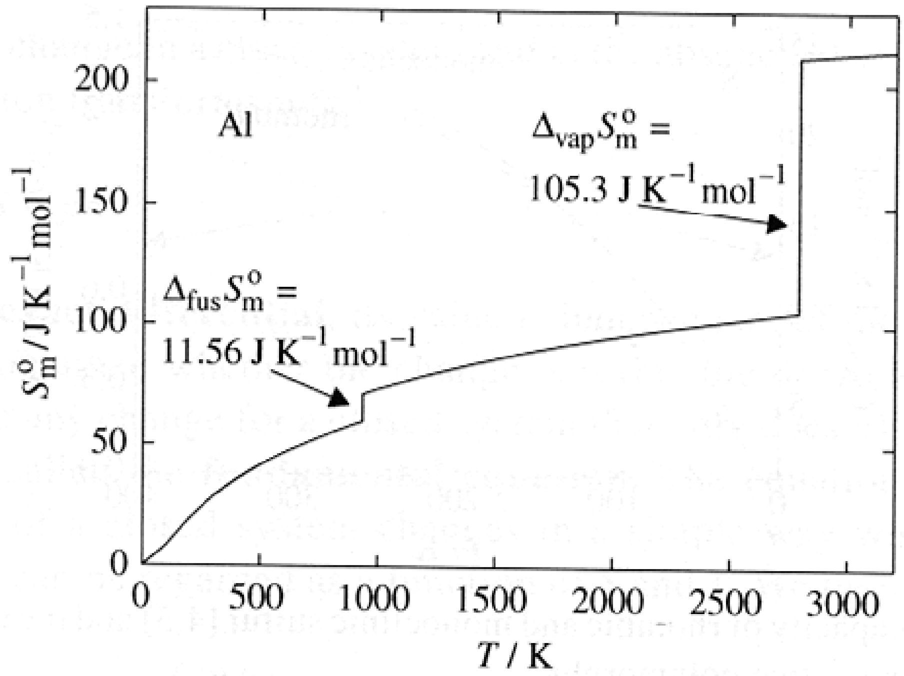

Figure 1.5 Standard entropy of aluminium relative to 0 K. The standard entropy of fusion ($\Delta_{fus}S_m^o$) is significantly smaller than the standard entropy of boiling ($\Delta_{vap}S_m^o$).

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Thermodynamic Functions… 1st Derivatives

- Temperature dependence of the Gibb's Free-Energy

$$\left(\frac{\partial G^{s}}{\partial T}\right)_{P} = -S^{s}$$

$$< \left(\frac{\partial G^{l}}{\partial T}\right)_{P} = -S^{l}$$

$$<< \left(\frac{\partial G^{g}}{\partial T}\right)_{P} = -S^{g}$$

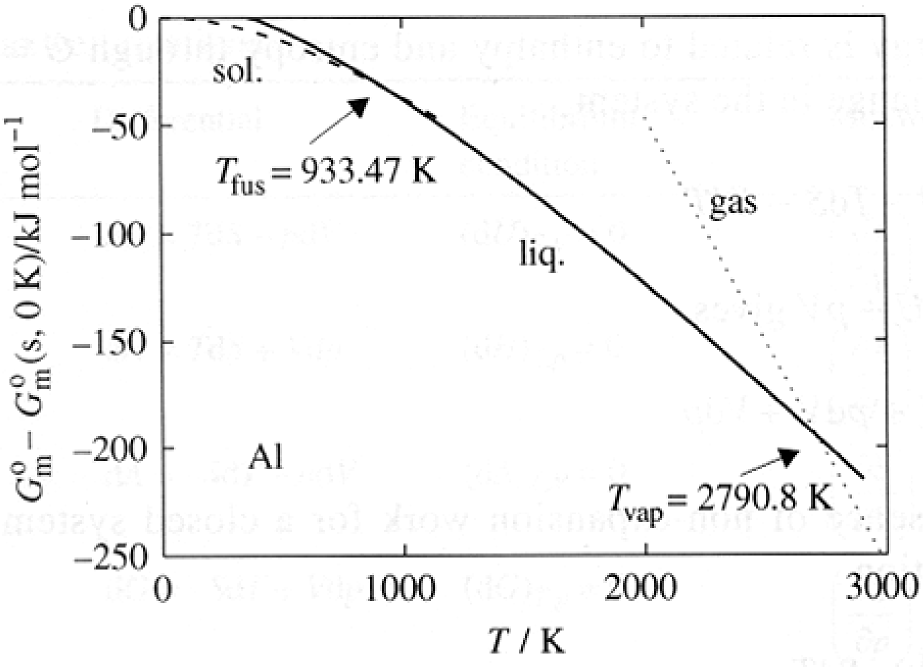

Figure 1.8 Standard Gibbs energy of solid, liquid and gaseous aluminium relative to the standard Gibbs energy of solid aluminium at $T = 0$ K as a function of temperature (at $p = 1$ bar).

Thermodynamic Functions… 1^{st} Derivatives

- $V^s < V^l < V^g$

$$\left(\frac{\partial G^s}{\partial P}\right)_T = V^s < \left(\frac{\partial G^l}{\partial P}\right)_T = V^l < \left(\frac{\partial G^g}{\partial P}\right)_T = V^g$$

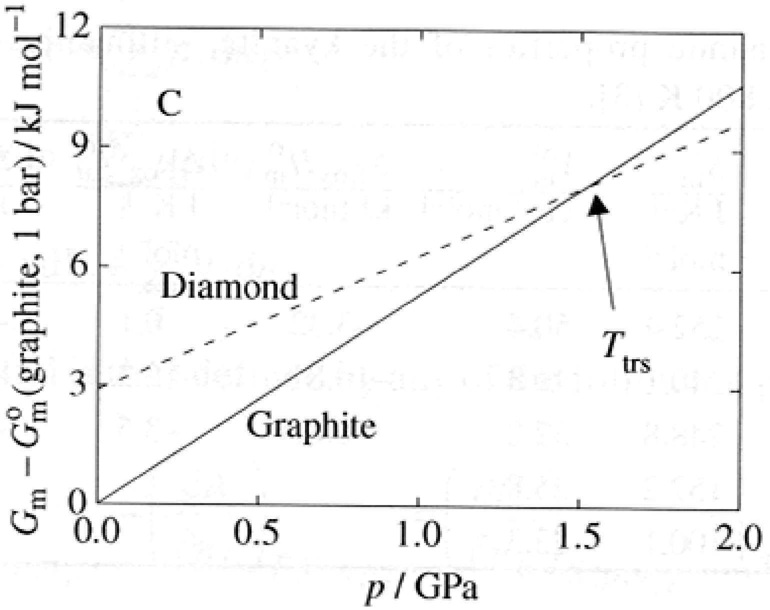

Figure 1.9 Standard Gibbs energy of graphite and diamond at $T = 298$ K relative to the standard Gibbs energy of graphite at 1 bar as a function of pressure.

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Thermodynamic Functions… 2nd Derivatives

- The thermodynamic functions we use are state functions, and state functions (variables) have the property of being exact
- That is, the formation of their second derivative is independent of the order of differentiation:

$$\left(\frac{\partial}{\partial x}\right)_y \left(\frac{\partial F(x,y)}{\partial y}\right)_x = \left(\frac{\partial}{\partial y}\right)_x \left(\frac{\partial F(x,y)}{\partial x}\right)_y$$

$$\left(\frac{\partial^2 F(x,y)}{\partial x \partial y}\right) = \left(\frac{\partial^2 F(x,y)}{\partial y \partial x}\right)$$

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Thermodynamic Functions… 2nd Derivatives

- When this is applied to thermodynamic functions, we call them the Maxwell relationships and we get the following:

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

- Exercise: There are four, write out the remaining three:

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

Thermodynamic Functions… 2nd Derivatives

- Maxwell Relations:

$$dU = TdS - PdV \qquad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$dH = TdS + VdP \qquad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$dA = -SdT - PdV \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$dG = -SdT + VdP \qquad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

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Thermodynamic Functions… 2^{nd} Derivatives

- Some are more useful than others…

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

$$dS_T = -\left(\frac{\partial V}{\partial T}\right)_P dP$$

$$\int_{S_1}^{S_2} dS = S_2 - S_1 \equiv S(P_2) - S(P_1) = \int_{V_1}^{V_2} \left(\frac{\partial V}{\partial T}\right)_V dP$$

Homework Exercise for next time:

- Derive an expression for the following quantity in terms of easily measured quantities and apply it to liquid B_2O_3 slightly above its melting point and crystalline B_2O_3 slightly below its melting point

$$\left(\frac{\partial S}{\partial V}\right)_P$$