**Homework 2 Advanced Thermodynamics**

**Due Tuesday September 7, 2020**

1. By performing a Legendre transformation show that –(**S/**P)T = (**V/**T)P. Start by obtaining an expression for dG from the definition of the Gibbs free energy, G = H – ST; obtaining an expression for dH from the definition of H, H = U + PV, and an expression for dU from dU = dq +dwec. Perform a Legendre transform with the expression for dG to obtain the desired Maxwell relationship.
2. Show how you can obtain the expressions for G, H, U; dG, dH, dU, and the final Maxwell expression from the thermodynamic square.
3. Han Guangze and Meng Jianjia, *Extension of Gibbs–Duhem equation including influences of external field* Continuum Mech. Thermodyn. (2018) **30** 817–823, wrote an expression extending the Gibbs-Duhem equation to include the influence of an external field such as gravity or an electric field, $SdT-Vdp+\sum\_{}^{}n\_{i}dμ\_{i}+\sum\_{}^{}Y\_{j}dX\_{j} $= 0, where X is an intensive property and Y is the corresponding extensive property. The energy postulate states that the differential of a form of energy is the intensive property, X, times the differential of the extensive property, Y. for instance for gravity (gh)dm; for surfaces dA; for and electric potential field dq, for polarization EdP’ (see the Guangze/Jianjia paper for definition of the terms). Ma, Gao, Qian and Su, *Size-dependent Electrochemical Propoerties of Binary Solid Solution Nanoparticles*, J. Elec. Soc. (2020) **167** 041501, proposed the following expression for the impact of particle size on electrical potential in nanoparticles,



Where F is the Faraday constant (charge per mole of electrons), Z is the moles of transferred electrons,  is electric potential. Does this expression agree with the proposed expression of Guangze and Jianjia? What is the origin of the ln() terms? What is the origin of the surface energy terms? How does the final term for electric potential relate to Guangze and Jianjia’s expression?

1. We obtained in class that CV = T(**S/**T)V. Show the origin of this expression, then use this expression to obtain an expression for (**CV/**V)T. You will need to change the order of differentiation and use a Maxwell relation. Provide an answer in T, P, V, and the tabulated derivatives , , Cp, CV, JT.
2. Find a value for (**CV/**T)V for an ideal gas, PV = RT where V is the molar volume, and for the van der Waals equation, P = RT/(V – b) – a/V (or Z = PV/RT = (1/(1-b/V)) – a/(VRT)). What does this tell you about an ideal gas, and about a van der Waals gas? You will need to define heat capacity in your explanation.

Answers: **Homework 2 Advanced Thermodynamics**

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**It should be the field not the potential, (dV/dr) not V**

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