School of Physics and Astronomy

Junior Honours **Thermodynamics** GJA 2019-2020

Tutorial 6: Thermodynamic potentials

1 Questions: Thermodynamic Potentials

1. **Heat Capacities**

   The heat capacity is *defined* as the amount of heat required to raise the temperature of a body by 1K. From this, the First Law and the Central Equation, prove that:

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

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

2. **Helmholtz function and pressure**

   Write down the differential form of the Helmholtz function $F = U - TS$, and an expression for pressure in terms of F.

   The specific Helmholtz function of a particular gas is:

   $$f = \frac{F}{n} = f_0(T) - \frac{a}{v} - RT\ln(v-b)$$

   where f_0 is a function of T only, while a and b are constants. Calculate the pressure of the gas, and hence its equation of state.

3. **EXAM STYLE QUESTION Using Maxwell relations**

   The Helmholtz thermodynamic potential F is defined by $F = U - TS$.

   Starting from the Central equation ($dU = -PdV + TdS$) and this definition, derive the Maxwell relation associated with the Helmholtz potential.

   For any material, the difference between the heat capacities at constant pressure and volume is given by

   $$C_P - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$$

   Using the Maxwell relation, show that

   $$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

   and that

   $$C_P - C_V = \frac{VT\beta_P^2}{\kappa_T}$$

   where β_P is the isobaric volume expansivity and κ_T is the isothermal compressibility.

   Use a similar technique to prove that the difference between the isothermal and the adiabatic compressibilities is

   $$\kappa_T - \kappa_S = \frac{TV\beta_P^2}{C_P}$$

   Verify that $C_P - C_V = R$ and $\kappa_T - \kappa_S$ for a monatomic ideal gas.

4. **A block of metal.**

   A block of metal is subjected to an adiabatic and reversible increase of pressure from P_1 to P_2. Show that the initial and final temperatures T_1 and T_2 are related by

   $$\ln(T_2/T_1) = V\beta(P_2 - P_1)/C_P$$

   You may assume that the volume of the block stays approximately constant during the compression. *Hint: Think about entropy S(P,T). What does reversible and adiabatic mean for entropy? Then try to obtain an expression involving T and P (the variables mentioned in the question...)*

5. **From Gibbs function to equation of state**

   A gas has molar Gibbs Free energy given by

   $$g = RT\ln P + A + BP + \frac{1}{2}CP^2 + \frac{1}{3}DP^3$$

   where A, B, C and D are constants. Find the equation of state (i.e. the relationship between P,V, and T) and explain why it is independent of A.

6. **A harmonic material**

   Suppose a material has an equation of state per kg given by

   $p = A(v - b) + CT$

   Given that at $P = 0$, T=300K: $v_0 = 10^{-3}m^3/kg$; $K_T = 10^{10}$Pa; $\beta = 10^{-5}K^{-1}$, determine the constants A, b, C? Is this a gas or a condensed phase?

7. **Challenge Question: Deriving the ideal gas equation from experimental laws.**

   Use *Joule's Law* (the internal energy of an ideal gas depends only on temperature) and *Boyle's Law* (at constant temperature, the product of pressure and volume for a fixed amount of an ideal gas is a constant), to derive the form of the equation of state of the ideal gas.
   Hint: start with the Central Equation, and employ one of the Maxwell relations. Then integrate...

Nonexaminable fun quiz: Violating the first Law with relativity

A 1000kg car accelerates from 0 to 10m/s, then from 10m/s to 20m/s. How much work does the engine do?

Simple Answer Work converts to kinetic energy, $\frac{1}{2}mv^2$. So in the first part we do $\frac{1}{2}.1000.10^2 = 50,000J$ and in the second part $\frac{1}{2}.1000.(20^2 - 10^2) = 150,000J$.

But, in Galilean relativity, we can consider the problem from the viewpoint of an observer moving at 10m/s. Relative to zim, the second phase is just accelerating from 0 to 10m/s, so the engine supplies only $50,000J$, saving 2/3rds of the fuel.

So, what went wrong?