

EP2827: Thermodynamics

Homework Set II*

February 22, 2020

1. A corollary which follows from the Carathéodory statement of the second law is,

In the space of thermodynamic equilibrium states, no two reversible adiabatic (hyper)surfaces can ever intersect.

Prove this by contradiction by repeating the argument in the class, i.e. if the opposite holds then the Kelvin-Planck version of the second law is violated. 5 points

2. In the lecture(s) while proving that the integrating factor for the heat pfaffian is a function of the temperature, θ , we set up a thought experiment where we had a composite system made up of a main system, A and reference system B . We deduced from the equations,

$$\frac{\lambda}{\Lambda} = \frac{\partial \Sigma}{\partial \sigma}, \quad \frac{\lambda'}{\Lambda} = \frac{\partial \Sigma}{\partial \sigma'}$$

that the integrating factors for the main system, the reference system and the composite system must be of the forms:

$$\lambda = \varphi(\theta) f(\sigma).$$

$$\lambda' = \varphi(\theta) f'(\sigma')$$

$$\Lambda = \varphi(\theta) g(\sigma, \sigma')$$

Prove that $g(\sigma, \sigma') = g(\Sigma(\sigma, \sigma'))$. Hint: Show that the Jacobian of the transformation from σ, σ' to $g(\sigma, \sigma'), \Sigma(\sigma, \sigma')$ vanishes. 5 points

3. Show that the following Pfaffian form (of three variables $x; y; z$) does not admit an integrating factor:

$$dF = xdy + kdz,$$

where k is a constant. (Hint: Refer to the note on exact and inexact differentials posted on the website). 5 points

4. For an ideal gas with constant heat capacities, show that:

A. The entropy can be given by the expression

$$S = C_V \ln P + C_P \ln V + \text{const.}$$

*Due in class on Wednesday, 28th Feb.

B. The adiabatic compressibility is

$$\kappa_S \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S = \frac{1}{\gamma P},$$

where $\gamma = C_P/C_V$.

5 + 2 = 7 points

5. For a paramagnetic ideal gas, obeying both the Curie's law and the ideal gas equation of state, show that the entropy is given by,

$$S = C_{V,M} \ln T + nR \ln V - \frac{\mu_0 M^2}{2C_C} + \text{const.},$$

where $C_{V,M}$ is the heat capacity at constant volume and magnetization, assumed constant, and C_C is the Curie constant. 5 points

6. A hydrostatic system of constant heat capacity, C_P and at a temperature T_i is put in contact with a reservoir at a higher temperature T_f . The pressure remains constant while the body comes to equilibrium with the reservoir. Show that the entropy change of the universe is equal to

$$C_P [x - \ln(1 + x)]$$

where $x = -(T_f - T_i)/T_f$. Prove that this entropy change is positive.

5 + 2 = 7 points

7. Show that for a hydrostatic system,

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

and,

$$\left(\frac{\partial H}{\partial P} \right)_T = -\mu C_P,$$

where $\mu \equiv \left(\frac{\partial T}{\partial P} \right)_H$ is the Joule-Thomson coefficient and H is the enthalpy of the system. For an ideal gas, $\mu = 0$. Show that for an ideal gas, $H = H(T)$, i.e. the enthalpy is purely a function of the temperature. 2 + 2 + 2 = 6 points