PHYS301
Homework 10 solutions

Spring 2026

Due: April 27th

Contents

Problem 1 [3 points]

Enthalphy: To create a system with total energy E on Earth, we not only need to provide the energy E but also the work needed to make room for it (e.g. displacing the air that used to be where the system now sits). At constant pressure P, this work is simply PV, where V is the volume of the newly created system. To take this into account, we define the enthalpy as $H = E + PV$.

a) Using the first law of thermodynamics with[a] $đQ = TdS$, show that $dH = TdS + VdP$.

b) The heat capacity at constant pressure C_P is defined as

$$C_P = \frac{đQ}{dT}\bigg|_P \tag{1}$$

Argue that this heat capacity is related to the enthalpy via

$$C_P = \frac{\partial H}{\partial T}\bigg|_P \tag{2}$$

[a] Where đ denotes an inexact differential, whereas exact differentials d are total derivatives.

a) Starting from the definition of enthalpy:

$$\begin{aligned} H &= E + PV \\ \text{(differential)} \quad dH &= dE + PdV + VdP \\ \text{(insert 1st law)} \quad dH &= (đQ + đW) + PdV + VdP \\ dH &= (TdS - \cancel{PdV}) + \cancel{PdV} + VdP \\ &= TdS + VdP \end{aligned} \tag{3}$$

as expected.

b) Assume constant pressure, so that $dP = 0$. Then the relation for enthalpy becomes

$$\begin{aligned} dH &= TdS + \cancel{VdP} \\ &= TdS \\ &= đQ \end{aligned} \tag{4}$$

Because $đQ = dH$, the definition of C_P can be rewritten as

$$C_P = \frac{\partial H}{\partial T}\bigg|_P \tag{5}$$

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Problem 2 [12 points]

Joule-Thomson process for cooling gases: Figure 1 below shows a thermally insulated pipe (i.e. no heat flow) which has a porous barrier separating two halves of the pipe. A gas of volume V_1, initially on the left-hand side of the pipe, is forced by a piston to go through the porous barrier using a constant pressure P_1. Assume the process can be treated quasistatically. As a result the gas flows to the right-hand side, resisted by another piston which applies a constant pressure P_2 ($P_2 < P_1$). Eventually all of the gas occupies a volume V_2 on the right-hand side.

a) Show that the enthalpy $H = E + PV$ is conserved in the Joule-Thomson process, where E is the total energy of the gas.

b) Define the Joule-Thomson coefficient as

$$\mu_{\rm JT} \equiv \frac{\partial T}{\partial P}\bigg|_H \tag{6}$$

Use enthalpy conservation ($dH = 0$) and the results from question 1 to show that this coefficient takes the form

$$\mu_{\rm JT} = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] \tag{7}$$

Note: You will need the following relation

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{8}$$

c) Compute $\mu_{\rm JT}$ for an ideal gas. Can the Joule-Thomson process be used to cool an ideal gas?

d) If we wish to use the Joule-Thomson process to cool a real (non-ideal) gas, what must the sign of $\mu_{\rm JT}$ be?

e) Derive $\mu_{\rm JT}$ for a gas obeying the van der Waals equation of state to leading order in the density N/V, where N is the number of gas particles. For what values of temperature T can the gas be cooled?

a) There are two *works* being done here (being careful of $\pm$ signs). The left piston does work on the gas, but the gas also does work on the right piston. Hence, the net work on the gas is the difference

$$W = P_1V_1 - P_2V_2 \tag{9}$$

With no heat flow, $đQ = 0$, the change in energy is solely due to work:

$$\Delta E = W \tag{10}$$

Combining these results, we see that

$$E_2 - E_1 = P_1V_1 - P_2V_2 \tag{11}$$

Which we can rearrange as

$$\begin{aligned} E_2 + P_2V_2 &= E_1 + P_1V_1 \\ \Rightarrow \quad H_2 &= H_1 \end{aligned} \tag{12}$$

And we conclude that enthalpy is conserved.

b) Consider conservation of enthalpy, $dH = 0$:

$$0 = TdS + VdP \tag{13}$$

With entropy S a function of T, P, it follows that

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \\ &= \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP \end{aligned} \tag{14}$$

(using the definition of C_P and the provided relation), then

$$0 = C_P dT + \left(V - T\left(\frac{\partial V}{\partial T}\right)_P\right) dP \tag{15}$$

Solving for dT/dP (now a partial derivative at constant H)

$$\begin{aligned} \mu_{\text{JT}} &\equiv \left(\frac{\partial T}{\partial P}\right)_H \\ &= \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] \end{aligned} \tag{16}$$

c) Consider an ideal gas, where $V(T, P)$ is given by

$$V = nR\frac{T}{P} \tag{17}$$

Then

$$\begin{aligned} \left(\frac{\partial V}{\partial T}\right)_P &= \frac{nR}{P} \\ &= \frac{V}{T} \end{aligned} \tag{18}$$

So the Joule-Thomson coefficient is

$$\begin{aligned} \mu_{\text{JT}}^{(\text{ideal})} &= \frac{1}{C_P}\left(T\frac{V}{T} - V\right) \\ &= 0 \end{aligned} \tag{19}$$

for an ideal gas. Hence we can't cool it: now matter how much we change pressure, $\mu_{\text{JT}} = 0$ tells us that the temperature will not change (hence wont' cool).

d) In the Joule-Thomson process, the gas's pressure goes down ($P_2 < P_1$), so the change in pressure is always negative. If we want temperature to drop, then the change in pressure is also negative. Negative over negative yields a positive coefficient, hence

$$\text{Cooling when...} \quad \mu_{\text{JT}} > 0 \tag{20}$$

e) Starting from the van der Waals gas equation of state

$$\begin{aligned} Nk_BT &= \left(P + \frac{N^2}{V^2}a\right)(V - Nb) \\ Nk_BT &= PV - NPb + \frac{N^2}{V}a - \frac{N^3}{V^2}ab \\ \text{(leading order in } N/V) \quad Nk_BT &= PV - NPb + \frac{N^2}{V}a \\ V &\simeq \frac{Nk_BT}{P} + Nb - \frac{aN}{k_BT} \end{aligned} \tag{21}$$

for constants a, b. Taking the T partial derivative, we find that

$$\mu_{\text{JT}} = \frac{N}{C_P}\left(\frac{2a}{k_BT} - b\right) \tag{22}$$

From (d) we know that cooling is possible whenever $\mu_{\text{JT}} > 0$, which translates to

$$\begin{aligned} \frac{2a}{k_BT} &> b \\ \Rightarrow \quad T &< \frac{2a}{k_Bb} \end{aligned} \tag{23}$$

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Problem 3 [5 points]

In the course of pumping up a bicycle tire, a liter of air at atmospheric pressure is compressed *adiabatically* to a pressure of 7 atm. (Air is mostly diatomic nitrogen and oxygen)

a) What is the final volume of this air after compression?

b) How much work is done in compressing the air?

c) If the temperature of the air is initially 300 Kelvin, what is the temperature after compression?

a) Recall that (worksheet 16)

$$PV^\gamma = \text{constant} \tag{24}$$

Where the adiabatic index for diatomic particles is $\gamma = 7/5$. Using $P_1 = 1$ atm and $V = 1$ liter, the final volume (in liters) is

$$\begin{aligned} P_1 V_1^\gamma &= P_2 V_2^\gamma \\ \Rightarrow \quad V_2 &= V_1 \left(P_1 / P_2 \right)^{1/\gamma} \\ &\approx 0.25 \text{ liters} \end{aligned} \tag{25}$$

b) Integration of the above equation shows that the work done for $(V_1, P_1) \to (V_2, P_2)$ adiabatically is

$$W = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1} \tag{26}$$

Noting that 1 atmosphere is $101,325$ Pa, and that 1 liter is equiavlent to 0.001 m^3, it follows that

$$W \approx -188 \text{ Joules} \tag{27}$$

c) Analogous to part (a), we have that adiabatic compression satisfies $TV^{\gamma-1} = \text{constant}$, hence

$$\begin{aligned} T_2 &= T_1 \left(\frac{V_1}{V_2} \right)^{\gamma - 1} \\ &\approx 523 \text{ Kelvin} \end{aligned} \tag{28}$$

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