

Q4001 Thermodynamics of Materials
Midterm Exam. Part I

Antonio Osamu Katagiri Tanaka - A01212611@itesm.mx

```
In [1]: from IPython.display import display, Image
display(Image(filename='./img/part1_directions.jpg'));
display(Image(filename='./img/1_0.jpg'));
display(Image(filename='./img/1_1.jpg'));
display(Image(filename='./img/1_2.jpg'));
display(Image(filename='./img/1_3.jpg'));
```

Please turn in the exam Tuesday, october 8th, before 6:00pm.

1. An ideal gas is originally confined to a volume V_1 in an insulated container of volume $V_1 + V_2$. The remainder of the container is evacuated. The partition is then removed and the gas expands to fill the entire container. If the initial temperature of the gas was T , what is the final temperature? What is the change in entropy? Justify your answer.
2. Demonstrate the following thermodynamic relations:

$$(a) \left(\frac{\partial T}{\partial P} \right)_S = \frac{\alpha VT}{C_P}$$

$$(b) \left(\frac{\partial T}{\partial P} \right)_H = -\frac{V}{C_P} (1 - \alpha T)$$

$$(c) \left(\frac{\partial H}{\partial S} \right)_V = T \left[1 + \frac{\alpha V}{\kappa_T C_V} \right]$$

3. A certain system is found to have a Gibbs free energy given by

$$\overline{G} = RT \ln \left[\frac{aP}{(RT)^{5/2}} \right]$$

where a and R are constants. Find the specific heat at constant pressure, \overline{C}_P .

4. For a system whose internal energy is given by:

$$U = k \frac{S^3}{V}$$

where k is a constant.

- (a) What are the units of k ?
 - (b) Find the equation of the adiabats in the P vs. V plane.
 - (c) Find the derived expressions for P and T .
 - (d) Write the equation of state for the system in terms of P , V and T .
5. The heat of melting of ice at 1 atm and 0°C is 6.01 kJ/mol. The density of ice under these conditions is 0.917 g/cm^3 and the density of water is 0.9998 g/cm^3 . If 1 mole of ice is melted under these conditions, what will be
 - (a) the work done?
 - (b) the change in internal energy?
 - (c) the change in entropy?

Mid-Term Exam

Antonio Osamu Katagiri Tanaka A01212611 - CEM

"I state that the work I am submitting for this exam is solely my own and that I have not shared it. I have not used information coming from any uncited source in my answers" AKT

- 1 The internal energy does not change ($\Delta U = 0$), which implies that $\Delta T = 0$.
Therefore, the process is adiabatic.

$$\underline{T_1 = T_2 = T}$$

Since it's adiabatic, $q = 0$ and $PV^\gamma = \text{constant}$

\hookrightarrow no degradation of energy occurs, since it's reversible $\therefore \Delta S = 0$

$$\begin{aligned} 2a \quad dS &= \left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV \Rightarrow \left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P = \frac{C_P}{T} \left(\frac{\partial T}{\partial V}\right)_P \\ &\therefore \left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \end{aligned}$$

From a Maxwell relationship: $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -\alpha V$

$$\text{So: } \left(\frac{\partial T}{\partial P}\right)_S = \frac{(\partial S / \partial P)_T}{(\partial S / \partial T)_P} = \frac{-\alpha V}{C_P / T} = -\frac{\alpha V T}{C_P}$$

$$2b \quad \left(\frac{\partial T}{\partial P}\right)_H = -\frac{(\partial H / \partial P)_T}{(\partial H / \partial T)_P} = -\frac{1}{C_P} \left(\frac{\partial H}{\partial P}\right)_T$$

$$dH = TdS + VdP$$

$$\begin{aligned} \left(\frac{\partial H}{\partial P}\right)_T &= T \left(\frac{\partial S}{\partial P}\right)_T + V(1) = T \left(-\left(\frac{\partial V}{\partial T}\right)_P\right) + V \\ &= V - T\alpha V \end{aligned}$$

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P} (V - T\alpha V) = \frac{V}{C_P} (1 - T\alpha)$$

2c) $H = H(T, V)$

$$dH = \left(\frac{\partial H}{\partial T} \right)_V dT + \left(\frac{\partial H}{\partial V} \right)_T dV$$

at constant volume: $\left(\frac{\partial H}{\partial S} \right)_V = \left(\frac{\partial H}{\partial T} \right)_V \left(\frac{\partial T}{\partial S} \right)_V$

from cyclic rule: $\left(\frac{\partial S}{\partial P} \right)_V = \left(\frac{\partial S}{\partial T} \right)_V \left(\frac{\partial T}{\partial P} \right)_V = \frac{C_V}{T} \left(\frac{\partial T}{\partial P} \right)_V$ $\swarrow S = S(P, V)$
 $\left(\frac{\partial T}{\partial S} \right)_V = \frac{T}{C_V}$

from enthalpy $H = U + PV$

$$\left(\frac{\partial H}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V + \left(\frac{\partial P}{\partial T} \right)_V V \quad \swarrow \left(\frac{\partial T}{\partial P} \right)_V = \frac{\beta_T}{\alpha} \quad \text{and } C_V = \left(\frac{\partial U}{\partial T} \right)_V$$

$$\left(\frac{\partial H}{\partial T} \right)_V = C_V + \frac{\alpha V}{\beta_T}$$

So: $\left(\frac{\partial H}{\partial S} \right)_V = \left[C_V + \frac{\alpha V}{\beta_T} \right] \left[\frac{T}{C_V} \right] = T + \frac{T \alpha V}{\beta_T} = T \left[1 + \frac{\alpha V}{\beta_T} \right]$

But $\beta_T = K_T C_V$

$$\left(\frac{\partial H}{\partial S} \right)_V = T \left[1 + \frac{\alpha V}{K_T C_V} \right]$$

3) $dG = -SdT + VdP$

$$\left(\frac{\partial G}{\partial T} \right)_P = -S \quad \text{@ constant pressure}$$

if $G = RT \ln \left(\frac{aP}{(RT)^{5/2}} \right) \Rightarrow \left(\frac{\partial G}{\partial T} \right)_P = -\frac{5}{2} R + R \ln \left(\frac{aP}{(RT)^{5/2}} \right) = -S$

So: $S = \frac{5}{2} R + R \ln \left(\frac{aP}{(RT)^{5/2}} \right)$

then: $S = S(T, P)$

$$dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP$$

at constant pressure, the 1st law gives $\left(\frac{\partial S}{\partial T} \right)_P = \frac{C_P}{T}$

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

$$\left(\frac{\partial S}{\partial T}\right)_P = R \frac{5}{2T}$$

$$\text{So: } C_p = T \left(R \frac{5}{2T} \right) = \frac{5}{2} R //$$

$$[4] \quad U = k \frac{S^3}{V}$$

$$\text{Say } U = U(P, T)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V,n} dT + \left(\frac{\partial U}{\partial V}\right)_{T,n} dV + \left(\frac{\partial U}{\partial n}\right)_{T,V}$$

$$[4a] \quad J = \frac{(JK^{-1})^3}{m^3} \text{ k-units}$$

$$\text{k-units} = \frac{J^3 K^3 m^3}{J^3} = \frac{K^3 m^3}{J^2} //$$

as S is in J per Kelvin
 V is in m^3
 U in Joules.

$$[4c] \quad U = k \frac{S^3}{V} \quad \text{where } U = nC_v \Delta T$$

$$nC_v T = k \frac{S^3}{V}$$

$$\frac{nRT}{1-\gamma} = \frac{kS^3}{V} \quad \text{for an ideal gas}$$

$$\frac{PV}{1-\gamma} = \frac{kS^3}{V}$$

$$P = \frac{(1-\gamma)kS^3}{V^2} //$$

$$U = \frac{kS^3}{V} \quad \text{where } S = nC_p T$$

$$\frac{nRT}{1-\gamma} = \frac{k(nC_p T)^3}{V} \quad \text{with } C_p = \frac{R\gamma}{1-\gamma}$$

$$\frac{nRT}{1-\gamma} = \frac{k \left(\frac{nT R \gamma}{1-\gamma} \right)^3}{V}$$

$$\frac{nRT}{1-\gamma} = \frac{k n^3 T^3 R^3 \gamma^3}{V (1-\gamma)^3}$$

$$\frac{nR V (1-\gamma)^{3/2}}{(1-\gamma) k n^3 R^3 \gamma^3} = \frac{T^3}{T} \Rightarrow T^2 = \frac{(1-\gamma)^2 V}{n^2 k R^2 \gamma^3}$$

$$T = \sqrt{\frac{V(1-\gamma)^2}{n^2 R^2 k \gamma^3}} //$$

4b] The adiabats of the ideal gas is $PV^\gamma = \text{constant}$

So, from P and V from 4c]

$$\underbrace{\left[\frac{(1-\gamma)KS^3}{V^2} \right]}_P \underbrace{\left[\frac{V(1-\gamma)^2}{n^2 R^2 K \gamma^3} \right]^\gamma}_V = \text{constant}$$

4d] $dU = dq + dw$
 $dU = Tds - PdV$

$$dU = Tds - \frac{(1-\gamma)KS^3}{V^2} dV //$$

5a] The work is defined by \rightarrow H_2O molecular weight = 18.015

$$w = PdV$$

$$w = (1 \text{ atm}) \left(\frac{18.015}{0.9998 \text{ g cm}^{-3}} - \frac{18.015}{0.917 \text{ g cm}^{-3}} \right) (0.001 \text{ L})$$

$$w = -1.63 \text{ L atm}$$

$$= -0.16 \text{ J} //$$

5c] $q = 6.01 \text{ kJ} \rightarrow$ as it's the heat of melting.

$$\Delta S = \frac{q}{T} = \frac{6.01 \text{ kJ}}{0^\circ \text{C}} = \underline{22.002 \frac{\text{J}}{\text{K}}} //$$

5b] $\Delta U = q - w = 6.01 \text{ kJ} - (-0.16 \text{ J})$
 $\Delta U = \underline{6010.16 \text{ J} //$

References:

- [1] Stolen, S., Grande, T., & Neil L., A. (2004). Chemical Thermodynamics of Materials - Macroscopic and Microscopic Aspects. (J. W. & S. Inc., Ed.). John Wiley & Sons Ltd
- [2] B. Gaskell, D., & E. Laughlin, D. (2018). Introduction to the Thermodynamics of Materials. (C. Press Ed.). Taylor & Francis Group
- [3] Mortimer G., R. (2013) Mathematics for Physical Chemistry. (A.P. of Elsevier, Ed.) (4th ed.) Amsterdam: British Library Cataloguing in Publication Data

Q4001 Thermodynamics of Materials Midterm Exam. Part II

Antonio Osamu Katagiri Tanaka - A01212611@itesm.mx

"I state that the work I am submitting for this exam is solely my own and that I have not shared it. I have not used information coming from any uncited source in my answers."


```
In [7]: display(Image(filename='./img/part2_directions.jpg'));
```

Q4001 Thermodynamics of Materials

Midterm Exam. Part II

October, 2019

Please turn in the exam Tuesday, october 9th, before 4:00pm.

6. The state equation of a new material is

$$P = \frac{aT^3}{V}$$

where a is a constant. The internal energy of the matter is

$$U = BT^n \ln \frac{V}{V_o} + f(T)$$

where B , n and V_o are all constants, $f(T)$ only depends on the temperature. Find B and n .

7. The molar entropy of an gas is given by

$$\overline{S} = \frac{1}{2} \left[\sigma + 5R \ln \overline{U} + 2R \ln \overline{V} \right]$$

- (a) Find \overline{C}_V and \overline{C}_P .

(b) Find α and κ_T .
8. A paramagnetic system in an uniform magnetic field \mathcal{H} is thermally insulated from the surroundings. It has an induced magnetization $M = a\mathcal{H}/T$ and a heat capacity $C_{\mathcal{H}} = b/T^2$ at constant \mathcal{H} , where a and b are constants and T is the temperature. How will the temperature of the system change when \mathcal{H} is quasi-statically reduced to zero? In order to have the final temperature change by a factor of 2 from the initial temperature, how strong should be the initial \mathcal{H} ?
9. Demonstrate that

$$\overline{C}_P - \overline{C}_V = \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P \quad \text{and that} \quad P + \left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V$$

and calculate $\overline{C}_P - \overline{C}_V$ for a van der Waals gas. Compare how much these values differ for He and CO₂ at $T = 200$ K and $\overline{V} = 0.2$ L mol⁻¹.

gas	$a/\text{atm L}^2 \text{mol}^{-2}$	$b/\text{L mol}^{-1}$
He	0.0346	0.0238
CO ₂	3.64	0.0427

10. A thermally conducting, uniform and homogeneous bar of length L , cross section A , density ρ and specific heat at constant pressure c_P is brought to a nonuniform temperature distribution by contact at one end with a hot reservoir at a temperature T_h and at the other end with a cold reservoir at a temperature T_c . The bar is removed from the reservoirs, thermally insulated and kept at constant pressure.
- (a) Determine the final temperature of the bar.

(b) Show that the change in entropy of the bar is

$$\Delta S = c_P \rho A L \left[1 + \ln T_f + \frac{T_c}{T_h - T_c} \ln T_c - \frac{T_h}{T_h - T_c} \ln T_h \right]$$

Q 6

The 1st law gives,

$$\begin{aligned}dU &= TdS - PdV \\dS &= \frac{dU + PdV}{T} \\dS &= \frac{dU}{T} + \frac{PdV}{T} \\dS &= \left[\frac{1}{T} \left(\frac{\partial U}{\partial V} \right)_T + \frac{P}{T} \right] dV + \frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_V dT\end{aligned}$$

$$\left(\frac{\partial U}{\partial V} \right)_T = \frac{BT^n}{V} \text{ and } \left(\frac{\partial U}{\partial T} \right)_V = f'(T) + BnT^{n-1} \ln \left(\frac{V}{V_0} \right)$$

So,

$$\begin{aligned}dS &= \left[\frac{1}{T} \frac{BT^n}{V} + \frac{\frac{aT^3}{V}}{T} \right] dV + \frac{1}{T} \left[f'(T) + BnT^{n-1} \ln \left(\frac{V}{V_0} \right) \right] dT \\dS &= \frac{BT^{n-1} + aT^2}{V} dV + \left[\frac{f'(T)}{T} + nBT^{n-2} \ln \left(\frac{V}{V_0} \right) \right] dT \\ \frac{\partial}{\partial T} \left(\frac{BT^{n-1} + aT^2}{V} \right) &= \frac{\partial}{\partial V} \left(\frac{f'(T)}{T} + nBT^{n-2} \ln \left(\frac{V}{V_0} \right) \right) \\ \frac{2aT + B(n-1)T^{n-2}}{V} &= \frac{BnT^{n-2}}{V} \\ 2aT &= BnT^{n-2} - B(n-1)T^{n-2} \\ 2aT &= BT^{n-2}\end{aligned}$$

$B = 2aT^{3-n}$

[1] Lim, Y.-K. (2019). Problems and Solutions on Thermodynamics and Statistical Mechanics. Journal of Chemical Information and Modeling, 53(9), 1689–1699. <https://doi.org/10.1017/CBO9781107415324.004>

Q 7

@ constant volume

$$dU = TdS - PdV$$
$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$$

From:

$$S = \frac{1}{2}[\sigma + 5R\ln U + 2R\ln V]$$
$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{5R}{2U}$$
$$U = \frac{5}{2}RT$$

From the c_v definition,

$$c_v = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial}{\partial T} \frac{5}{2}RT = \frac{5R}{2}$$

From the c_p definition,

$$c_p = c_v + R = \frac{5R}{2} + R = \frac{7R}{2}$$

From Problem 9,

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

with:

$$\alpha = \frac{1}{v} \left(\frac{\partial V}{\partial T}\right)_P$$
$$P = -\left(\frac{\partial A}{\partial V}\right)_T$$
$$c_p - c_v = \alpha V \left[\left(\frac{\partial U}{\partial V}\right)_T - \left(\frac{\partial A}{\partial V}\right)_T\right]$$

$$A = U - TS$$
$$\left(\frac{\partial A}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T - T\left(\frac{\partial S}{\partial V}\right)_T$$
$$-\left(\frac{\partial A}{\partial V}\right)_T = -\left(\frac{\partial U}{\partial V}\right)_T + T\left(\frac{\partial S}{\partial V}\right)_T$$

$$c_p - c_v = \alpha V \left[T\left(\frac{\partial S}{\partial V}\right)_T\right] = T\alpha V \left(\frac{\partial P}{\partial T}\right)_V$$

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

$$c_p - c_v = T\alpha V \left[-\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P\right]$$
$$c_p - c_v = (T\alpha V) \left(\frac{1}{Vk_T}\right) (V\alpha)$$
$$c_p - c_v = \frac{VT\alpha^2}{k_T}$$
$$\frac{\alpha}{k_T} = \frac{R}{TV\alpha}$$

Since

$$\frac{\alpha}{k_T} = \frac{R}{V} = \frac{R}{TV\alpha}$$

$$\alpha = \frac{1}{T}$$

$$k_T = \frac{VT\alpha^2}{c_p - c_v}$$

$$k_T = \frac{VT\alpha^2}{R}$$

$$k_T = \frac{V}{RT}$$

[1] Lim, Y.-K. (2019). Problems and Solutions on Thermodynamics and Statistical Mechanics. Journal of Chemical Information and Modeling, 53(9), 1689–1699. <https://doi.org/10.1017/CBO9781107415324.004>

[2] R. Gaskell, D., & E. Laughlin, D. (2018). Introcuction to the Thermodynamics of Materials. (C. Press, Ed.). Taylor & Francis Group.

Q 8

$$dU = TdS + HdM$$

gives:

$$\left(\frac{\partial T}{\partial M}\right)_S = \left(\frac{\partial H}{\partial S}\right)_M$$

From a Maxwell relation:

$$\left(\frac{\partial T}{\partial S}\right)_H \left(\frac{\partial M}{\partial H}\right)_H = -1$$

Also:

$$c_H = T\left(\frac{\partial S}{\partial T}\right)_H$$

$$\left(\frac{\partial T}{\partial S}\right)_H = \frac{T}{c_H}$$

Recall:

$$M = \frac{aH}{T}$$

$$\left(\frac{\partial M}{\partial T}\right)_H = -\frac{aH}{T^2}$$

$$\left(\frac{\partial T}{\partial H}\right)_S = \left(\frac{\partial T}{\partial S}\right) \left(\frac{\partial S}{\partial H}\right) = \left(\frac{\partial H}{\partial S}\right) \left(\frac{\partial T}{\partial H}\right) \cdot \left(\frac{\partial H}{\partial T}\right) \left(\frac{\partial M}{\partial H}\right) \cdot \left(\frac{\partial T}{\partial S}\right) \left(\frac{\partial M}{\partial H}\right)$$

$$\left(\frac{\partial T}{\partial H}\right)_S = \left(\frac{\partial T}{\partial S}\right)_H \left(\frac{\partial M}{\partial T}\right)_H (-1)$$

$$\left(\frac{\partial T}{\partial H}\right)_S = -\frac{T}{c_H} \frac{aH}{T^2}$$

$$\left(\frac{\partial T}{\partial H}\right)_S = \frac{aTH}{b}$$

$$\int \frac{aHT}{b} dH = \frac{aH^2T}{2b} = \ln\left(\frac{T}{T_f}\right)$$

$$T = T_f \left(e^{\frac{aH^2T}{2b}}\right)$$

T approaches T_f when H approaches 0. If

$$T_f = \frac{T_i}{2}$$

Then

$$H_i = \left(\frac{2b}{a} \ln(2)\right)^{\frac{1}{2}}$$

[1] Lim, Y.-K. (2019). Problems and Solutions on Thermodynamics and Statistical Mechanics. Journal of Chemical Information and Modeling, 53(9), 1689–1699. <https://doi.org/10.1017/CBO9781107415324.004>

[3] R.L., C. (1986). Thermodynamics, Magnetoche(Springer), 3–4. Retrieved from https://link.springer.com/chapter/10.1007%2F978-3-642-70733-9_3

Q 9

Let's demonstrate: $\bar{C}_P - \bar{C}_V = \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P$

For a constant volume process ($w = 0$), the 1st Law gives:

$$dU = \delta q_v$$

From the definition of enthalpy:

$$dH = dU + PdV + VdP$$

@ constant pressure:

$$\begin{aligned} dH &= dU + PdV \\ dH &= \delta q_p \end{aligned}$$

From the definition of c_v and c_p ,

$$\begin{aligned} c_v &= \left(\frac{\delta q}{dT} \right)_v = \left(\frac{\partial U}{\partial T} \right)_v, \text{ as } dU = c_v dT \\ c_p &= \left(\frac{\delta q}{dT} \right)_p = \left(\frac{\partial H}{\partial T} \right)_p, \text{ as } dH = c_p dT \end{aligned}$$

If the process is carried out at constant volume, all the thermal energy is used to raise the temperature of the system.

If the process is carried out at constant pressure, some thermal energy is used to raise the temperature of the system and some is used to provide the work required to expand the system.

$$\frac{PdV}{dT} = P \left(\frac{\partial V}{\partial T} \right)_p \text{ is the work of expansion}$$

So, it's expected c_p to be greater than c_v . Therefore:

$$c_p - c_v = P \left(\frac{\partial V}{\partial T} \right)_p$$

From the definition of enthalpy:

$$\begin{aligned} H &= U + PV \\ dH &= dU + PdV + VdP \\ dH &= dU + PdV \text{ @ constant pressure} \\ \left(\frac{\partial H}{\partial T} \right)_p &= \left(\frac{\partial U}{\partial T} \right)_p + P \left(\frac{\partial V}{\partial T} \right)_p \end{aligned}$$

So:

$$c_p = \left(\frac{\partial H}{\partial T} \right)_p = \left(\frac{\partial U}{\partial T} \right)_p + P \left(\frac{\partial V}{\partial T} \right)_p$$

And:

$$c_v = \left(\frac{\partial U}{\partial T} \right)_v$$

For any gas

$$c_p - c_v = \left(\frac{\partial U}{\partial T} \right)_p + P \left(\frac{\partial V}{\partial T} \right)_p - \left(\frac{\partial U}{\partial T} \right)_v$$

$$\begin{aligned} U &= U(V, T) \\ dU &= \left(\frac{\partial U}{\partial V} \right)_T dV + \left(\frac{\partial U}{\partial T} \right)_V dT \\ \left(\frac{\partial U}{\partial T} \right)_P &= \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + \left(\frac{\partial U}{\partial T} \right)_V \end{aligned} \tag{1}$$

So,

$$\begin{aligned} c_p - c_v &= \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + \left(\frac{\partial U}{\partial T} \right)_V + P \left(\frac{\partial V}{\partial T} \right)_P - \left(\frac{\partial U}{\partial T} \right)_V \\ c_p - c_v &= \left(\frac{\partial U}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \end{aligned}$$

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

Let's demonstrate: $P + \left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V$

For one mole in a closed system:

$$\begin{aligned}dU &= TdS - PdV \\ \left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial S}{\partial V}\right)_T - P \quad (1) \\ \text{using the Maxwell relation: } \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V \\ \left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial P}{\partial T}\right)_V - P\end{aligned}$$

$$\left(\frac{\partial U}{\partial V}\right)_T + P = T\left(\frac{\partial P}{\partial T}\right)_V$$

Let's calculate $\bar{C}_P - \bar{C}_V$ for a van der Waals gas.

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Differentiate with respect to T (P constant)

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

From the definitios of the heat capacities:

$$\begin{aligned}c_v &= T\left(\frac{\partial S}{\partial T}\right)_V \text{ and } c_p = T\left(\frac{\partial S}{\partial T}\right)_P \\ \frac{c_p - c_v}{T} &= \left(\frac{\partial S}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_V \\ \frac{c_p - c_v}{T} &= \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_V \\ \frac{c_p - c_v}{T} &= \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P\end{aligned}$$

Maxwell relationship:

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

The Cycle Rule:

$$\begin{aligned}\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T &= -1 \\ \left(\frac{\partial V}{\partial T}\right)_P &= -\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T\end{aligned}$$

So:

$$\begin{aligned}\frac{c_p - c_v}{T} &= \left(\frac{\partial P}{\partial T}\right)_V \left[-\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial P}\right)_T \right] \\ c_p - c_v &= -T \frac{\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial P}{\partial V}\right)_T}\end{aligned}$$

For a van der Waals gas,

$$\begin{aligned}P &= \frac{RT}{V-b} - \frac{a^2}{V^2} \\ \left(\frac{\partial P}{\partial T}\right)_V &= \frac{R}{V-b} \text{ and } \left(\frac{\partial P}{\partial V}\right)_T = \frac{2a^2}{V^3} - \frac{RT}{(V-b)^2}\end{aligned}$$

Thus,

$$c_p - c_v = -T \frac{\left(\frac{R}{V-b}\right)^2}{\frac{2a^2}{V^3} - \frac{RT}{(V-b)^2}}$$

$$c_p - c_v = \frac{R^2TV^3}{-2a^2(V-b)^2 + RTV^3}$$

Let's compare $c_p - c_v$ for He and CO_2

```
In [1]: def Cp_min_Cv(T, V, R, a, b):
        numer = (R**2)*T*(V**3);
        denom = -2*(a**2)*(V - b)**2 + R*T*(V**3);
        return numer / denom;

# constants
T = 200; #K
V = 0.2; #L/mol
R = 0.082057; #L atm/K mol

# for He
a = 0.0346; #atm L^2/mol^2
b = 0.0238; #L/mol
He_Cp_min_Cv = Cp_min_Cv(T, V, R, a, b)

# for CO2
a = 3.64; #atm L^2/mol^2
b = 0.0427; #L/mol
CO2_Cp_min_Cv = Cp_min_Cv(T, V, R, a, b)

print("gas    Cp_min_Cv")
print("-----")
print("{}    {:>5.3f} {}".format("He ", He_Cp_min_Cv, "L atm/K mol"))
print("{}    {:>5.3f} {}".format("CO2", CO2_Cp_min_Cv, "L atm/K mol"))

gas    Cp_min_Cv
-----
He      0.082 L atm/K mol
CO2    -0.021 L atm/K mol
```

The values differ by $0.082 - (-0.021) = 0.103 \frac{Latm}{Kmol}$

[1] R. Gaskell, D., & E. Laughlin, D. (2018). Introcuction to the Thermodynamics of Materials. (C. Press, Ed.). Taylor & Francis Group.
[2] Berberan-santos, M. N. (2008). The van der Waals equation : analytical and approximate solutions, 43(4), 1437–1457. <https://doi.org/10.1007/s10910-007-9272-4>

Q 10

$\frac{T_H - T_C}{L}$ is the bar temperature gradient

$T_x = T_C + \frac{(T_H - T_C)x}{L}$ is the temperature at the cross section at distance x

Since the process is isobaric ans adiabatic,

$$\int_0^L \rho c_p \left[T_C + \frac{(T_H - T_C)x}{L} - T_f \right] dx = 0$$
$$\frac{1}{2} L \rho c_p T_C - L \rho c_p T_f + \frac{1}{2} L \rho c_p T_H = 0$$
$$\frac{1}{2} T_C - T_f + \frac{1}{2} T_H = 0$$

$$T_f = \frac{T_H + T_C}{2}$$

Let's calculate the change in entropy

$$\Delta S = c_p \rho A \int_0^L dx \int_{T_x}^{T_f} \frac{dT}{T}$$
$$\Delta S = c_p \rho A L \left[\ln \left(\frac{T_H + T_C}{2} \right) - \ln \left(T_C + \frac{(T_H - T_C)x}{L} \right) \right]$$

$$\Delta S = c_p \rho A L \left[1 + \ln \left(\frac{T_H + T_C}{2} \right) + \frac{T_C}{T_H - T_C} \ln(T_C) - \frac{T_H}{T_H - T_C} \ln(T_H) \right]$$

[1] Lim, Y.-K. (2019). Problems and Solutions on Thermodynamics and Statistical Mechanics. Journal of Chemical Information and Modeling, 53(9), 1689–1699. <https://doi.org/10.1017/CBO9781107415324.004>

In []: