

1 Process $P = AT^b$

A process on an ideal gas is defined by

$$P = AT^b.$$

Express this process in terms of (P, V) and (V, T) . Calculate compressibility and thermal expansivity in this process. What is the limitation on b ? For which values of b this process becomes a known process? Find adiabatic values of the two thermodynamic coefficients above.

Solution: Using the equation of state of the ideal gas

$$PV = \nu RT,$$

one obtains

$$P = A \left(\frac{PV}{\nu R} \right)^b.$$

This can be represented in the simplified form

$$P^{1-1/b} V = \nu R / A^{1/b}.$$

Another form of this process reads

$$\frac{\nu RT}{V} = AT^b$$

that can be simplified to

$$T^{b-1} V = \nu R / A.$$

Compressibility is given by

$$\kappa = -\frac{1}{V} \frac{dV}{dP}.$$

Using $V \propto P^{-(1-1/b)}$ above, one obtains

$$\kappa = \left(1 - \frac{1}{b}\right) \frac{P^{-(1-1/b)-1}}{V} = \left(1 - \frac{1}{b}\right) \frac{1}{P}.$$

Since mechanical stability requires $\kappa > 0$, the condition on b is $b > 1$ or $b < 0$.

Thermal expansion coefficient is defined by

$$\beta = \frac{1}{V} \frac{dV}{dT}.$$

Using $V \propto T^{-(b-1)}$ above, one obtains

$$\beta = \frac{1-b}{T}.$$

Identification with known processes. Isobaric process: $b = 0$; isochoric process: $b = 1$; isothermic process: $b \rightarrow \infty$; adiabatic process: $b = \gamma/(\gamma - 1) > 1$. From the latter one obtains adiabatic thermodynamic coefficients

$$\kappa_S = \frac{1}{\gamma P}, \quad \beta_S = -\frac{1}{(\gamma - 1) T},$$

that has to be compared with

$$\kappa_T = \frac{1}{P}, \quad \beta_P = \frac{1}{T}.$$

Note that $\beta_S < 0$ because in the adiabatic process the volume decreases and the temperature increases.

2 Work and heat in the $P = AT^2$ process

A process on an ideal gas is defined by

$$P = AT^2, \quad A = \text{const.}$$

Calculate the received work and heat upon changing the temperature from T_1 to T_2 . Assume $C_V = \text{const.}$

Solution: Use the equation of state of the ideal gas

$$PV = \nu RT$$

to express P in terms of V as

$$P = \frac{(\nu R)^2}{AV^2}$$

and integrate

$$W_{12} = - \int_1^2 P dV = - \int_1^2 \frac{(\nu R)^2}{AV^2} dV = \frac{(\nu R)^2}{A} \left(\frac{1}{V_2} - \frac{1}{V_1} \right).$$

Then express V via T ,

$$V = \frac{\nu RT}{P} = \frac{\nu RT}{AT^2} = \frac{\nu R}{AT},$$

and substitute it into the work,

$$W_{12} = \nu R(T_2 - T_1).$$

To calculate the heat, use the first law of thermodynamics in the form

$$U_2 - U_1 = Q_{12} + W_{12}.$$

Using

$$U = C_V T + \text{const}$$

for a perfect gas and the result for the work, one obtains

$$Q_{12} = C_V(T_2 - T_1) - W_{12} = (C_V - \nu R)(T_2 - T_1).$$

3 Heat capacity in the process $P = AT^b$

Calculate the heat capacity in the process

$$P = AT^b$$

of an ideal gas, expressing it as a function of T . Analyze different cases of b .

Solution: Use the first law of thermodynamics

$$dU = \delta Q - PdV.$$

The infinitesimal received heat is given by

$$\delta Q = dU + PdV = \left(\frac{\partial U}{\partial T} \right)_V dT + \left[\left(\frac{\partial U}{\partial V} \right)_T + P \right] dV.$$

One has

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

while for the ideal gas $\left(\frac{\partial U}{\partial V} \right)_T = 0$. Thus the expression above simplifies to

$$\delta Q = C_V dT + PdV.$$

Now one has to express dV through dT . From the equation of the process and the equation of state of the ideal gas one obtains

$$V = \frac{\nu R}{A} T^{1-b}.$$

From here follows

$$dV = \frac{\nu R}{A} (1-b) T^{-b} dT.$$

With the help of the process equation this yields

$$\delta Q = C_V dT + \nu R(1-b) dT$$

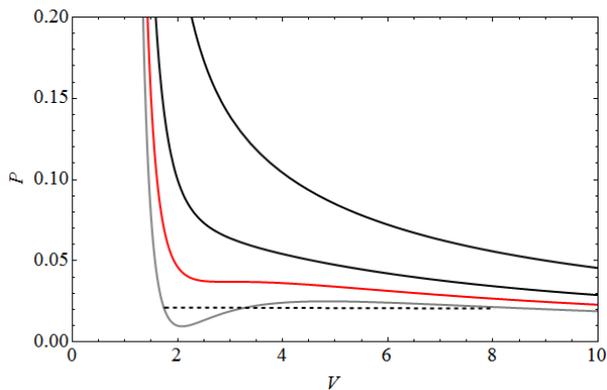


Figure 1: Isotherms of the van der Waals gas.

and, finally,

$$C = \frac{\delta Q}{dT} = C_V + \nu R(1 - b).$$

From here for the isobaric process, $b = 0$, one obtains $C = C_P = C_V + \nu R$ (Meyer's relation). For the isochoric process, $b = 1$, one obtains $C = C_V$. For the isothermic process, $b \rightarrow \infty$, one obtains $C \rightarrow \infty$. For the adiabatic process, $b = \gamma/(\gamma - 1)$, where $\gamma = C_P/C_V$, one obtains

$$C = C_V - \frac{\nu R}{\gamma - 1} = \frac{C_V \left(\frac{C_P}{C_V} - 1 \right) - \nu R}{\gamma - 1} = \frac{C_P - C_V - \nu R}{\gamma - 1} = 0,$$

taking into account Meyer's relation above.

4 Van der Waals gas

Van der Waals equation of state for a non-ideal gas describing its transition to liquid has the form

$$\left(P + \frac{a}{V^2} \right) (V - b) = \nu RT,$$

where a describes attraction of the gas molecules and b describes the volume occupied by the molecules and thus excluded from their motion.

1. Using a plotting program or by hand, plot isotherms of this gas for different T , setting $a = b = \nu R = 1$. At high T isotherms are close to those for an ideal gas but for lower T they become distorted. Finally at some $T = T_c$ (critical temperature) the isotherm becomes horizontal at some point called "critical point", where its second derivative also turns to zero.
2. Calculate the isothermal compressibility of the van der Waals gas in terms of (V, T) . Obtain its high-temperature limit. What happens with it at the critical point?
3. Find the critical point parameters using the analysis in (1.) as a hint.

Solution: Represent the compressibility in the form

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \left(\frac{\partial P}{\partial V} \right)_T^{-1}$$

and resolve the equation of state for P as

$$P = \frac{\nu RT}{V - b} - \frac{a}{V^2}.$$

One can see that the b -term increases pressure whereas the a -term decreases pressure, as expected. Differentiating P one obtains

$$\left(\frac{\partial P}{\partial V} \right)_T = -\frac{\nu RT}{(V - b)^2} + \frac{2a}{V^3}$$

that yields

$$\kappa_T = -\frac{1}{V} \frac{1}{-\frac{\nu RT}{(V - b)^2} + \frac{2a}{V^3}} = \frac{(V - b)^2 / V}{\nu RT - 2a(V - b) / V^3}.$$

At high temperatures V becomes large, so that one can neglect the terms with a and b and obtains $\kappa_T = V/(\nu RT) = 1/P$ that is the result for an ideal gas. With lowering T , the volume decreases and the negative term in the denominator causes κ_T to diverge at the critical point.

To find the critical point, one can use $(\frac{\partial P}{\partial V})_T = (\frac{\partial^2 P}{\partial V^2})_T = 0$, that is,

$$\begin{aligned}\left(\frac{\partial P}{\partial V}\right)_T &= -\frac{\nu RT}{(V-b)^2} + \frac{2a}{V^3} = 0 \\ \left(\frac{\partial^2 P}{\partial V^2}\right)_T &= \frac{2\nu RT}{(V-b)^3} - \frac{6a}{V^4} = 0.\end{aligned}$$

Getting rid of the denominators, one obtains the system of equations

$$\begin{aligned}\nu RTV^3 &= 2a(V-b)^2 \\ \nu RTV^4 &= 3a(V-b)^3.\end{aligned}$$

Dividing the second equation by the first one yields

$$V = (3/2)(V-b).$$

Solving this equation, one obtains the critical volume

$$V_c = 3b.$$

After that one obtains the critical temperature

$$\nu RT_c = \frac{2a}{V_c^3} (V_c - b)^2 = \frac{8a}{27b}.$$

Finally, the critical pressure can be obtained from the equation of state,

$$P_c = \frac{\nu RT_c}{V_c - b} - \frac{a}{V_c^2} = \frac{8a}{27b \times 2b} - \frac{a}{(3b)^2} = \frac{a}{27b^2}.$$

5 Isochore-isotherm cycle

Find the efficiency of a heat machine using a isochore-isotherm cycle of an ideal gas.

Solution: The cycle is similar to the Carnot cycle with the adiabats replaced by isochores, and it is performed in the clockwise direction. The heat is received by the system at the upward isochore, $Q'_2 = Q_{DA}$ and rightbound isotherm, $Q''_2 = Q_{AB}$. The heat is given away on the downward isochore, $Q'_1 = -Q_{BC}$ and leftbound isotherm, $Q''_1 = -Q_{CD}$. The efficiency is given by

$$\eta = \frac{Q_2 - Q_1}{Q_2}, \quad Q_1 = Q'_1 + Q''_1, \quad Q_2 = Q'_2 + Q''_2.$$

The heat on isochores can be calculated via the change of the internal energy, because there is no work:

$$Q'_2 = Q_{DA} = C_V (T_2 - T_1), \quad Q'_1 = -Q_{BC} = C_V (T_2 - T_1).$$

The heat on the isotherms can be calculated via the work done, because the internal energy does not change:

$$\begin{aligned}Q''_2 &= Q_{AB} = -W_{AB} = -\nu RT_2 \ln \frac{V_A}{V_B} = \nu RT_2 \ln \frac{V_B}{V_A} \\ Q''_1 &= -Q_{CD} = W_{CD} = \nu RT_1 \ln \frac{V_C}{V_D} = \nu RT_1 \ln \frac{V_B}{V_A}.\end{aligned}$$

Now one obtains

$$\eta = \frac{\nu RT_2 \ln \frac{V_B}{V_A} + C_V (T_2 - T_1) - \nu RT_1 \ln \frac{V_B}{V_A} - C_V (T_2 - T_1)}{\nu RT_2 \ln \frac{V_B}{V_A} + C_V (T_2 - T_1)}$$

that simplifies to

$$\eta = \frac{T_2 - T_1}{T_2 + C_V (T_2 - T_1) / \left(\nu R \ln \frac{V_B}{V_A}\right)}.$$

one can see that because of the additional positive term on the denominator, the efficiency is smaller than the efficiency of the Carnot cycle, $\eta = (T_2 - T_1)/T_2$.