

3.3. MAXWELL RELATIONS AND SECONDARY PROPERTIES

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$$= \sqrt{RT \left(1 + \frac{R}{c_v}\right)} \quad (3.106)$$

$$= \sqrt{RT \left(1 + \frac{c_P - c_v}{c_v}\right)} \quad (3.107)$$

$$= \sqrt{RT \left(\frac{c_v + c_P - c_v}{c_v}\right)} \quad (3.108)$$

$$= \sqrt{\gamma RT} \quad (3.109)$$

Sound speed depends on temperature alone for the calorically perfect ideal gas.

Example 3.5**Virial Gas**

Find the sound speed if

$$P(T, \rho) = \rho RT (1 + b_1 \rho) \quad (3.110)$$

The necessary partials are

$$\left. \frac{\partial P}{\partial \rho} \right|_T = RT + 2b_1 \rho RT \quad \left. \frac{\partial P}{\partial T} \right|_\rho = \rho R (1 + b_1 \rho) \quad (3.111)$$

so

$$c(T, \rho) = \sqrt{RT + 2b_1 \rho RT + \frac{T}{c_v \rho^2} (\rho R (1 + b_1 \rho))^2} \quad (3.112)$$

$$= \sqrt{RT \left(1 + 2b_1 \rho + \frac{R}{c_v} (1 + b_1 \rho)^2\right)} \quad (3.113)$$

Sound speed depends on both temperature **and** density.

Example 3.6

Thermodynamic process with a van der Waals Gas

A van der Waals gas with

$$R = 200 \text{ J/kg/K} \quad (3.114)$$

$$a = 150 \text{ Pa m}^6/\text{kg}^2 \quad (3.115)$$

$$b = 0.001 \text{ m}^3/\text{kg} \quad (3.116)$$

$$c_v = [350 + 0.2(T - 300K)] \text{ J/kg/K} \quad (3.117)$$

begins at $T_1 = 300\text{ K}$, $P_1 = 1 \times 10^5\text{ Pa}$. It is isothermally compressed to state 2 where $P_2 = 1 \times 10^6\text{ Pa}$. It is then isochorically heated to state 3 where $T_3 = 1,000\text{ K}$. Find w_{13} , q_{13} , and $s_3 - s_1$. Assume the surroundings are at $1,000\text{ K}$. Recall

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \quad (3.118)$$

so at state 1

$$100,000 = \frac{200 \times 300}{v_1 - 0.001} - \frac{150}{v_1^2} \quad (3.119)$$

or expanding

$$-0.15 + 150v - 60,100v^2 + 100,000v^3 = 0 \quad (3.120)$$

Cubic equation—three solutions:

$$v_1 = 0.598\text{ m}^3/\text{kg} \quad (3.121)$$

$$v_1 = 0.00125 - 0.0097i\text{ m}^3/\text{kg} \quad \text{not physical} \quad (3.122)$$

$$v_1 = 0.00125 + 0.0097i\text{ m}^3/\text{kg} \quad \text{not physical} \quad (3.123)$$

Now at state 2 we know P_2 and T_2 so we can determine v_2

$$1,000,000 = \frac{200 \times 300}{v_2 - 0.001} - \frac{150}{v_2^2} \quad (3.124)$$

The physical solution is $v_2 = 0.0585\text{ m}^3/\text{kg}$. Now at state 3 we know $v_3 = v_2$ and T_3 . Determine P_3 :

$$P_3 = \frac{200 \times 1,000}{0.0585 - 0.001} - \frac{150}{0.0585^2} = 3,478,261 - 43,831 = 3,434,430\text{ Pa} \quad (3.125)$$

Now $w_{13} = w_{12} + w_{23} = \int_1^2 P dv + \int_2^3 P dv = \int_1^2 P dv$ since 2–3 is at constant volume. So

$$w_{13} = \int_{v_1}^{v_2} \left(\frac{RT}{v-b} - \frac{a}{v^2} \right) dv \quad (3.126)$$

$$= RT_1 \int_{v_1}^{v_2} \frac{dv}{v-b} - a \int_{v_1}^{v_2} \frac{dv}{v^2} \quad (3.127)$$

$$= RT_1 \ln \left(\frac{v_2 - b}{v_1 - b} \right) + a \left(\frac{1}{v_2} - \frac{1}{v_1} \right) \quad (3.128)$$

$$= 200 \times 300 \ln \left(\frac{0.0585 - 0.001}{0.598 - 0.001} \right) + 150 \left(\frac{1}{0.0585} - \frac{1}{0.598} \right) \quad (3.129)$$

$$= -140,408 + 2,313 \quad (3.130)$$

$$= -138,095\text{ J/kg} = -138\text{ kJ/kg} \quad (3.131)$$

The gas is compressed, so the work is negative. Since e is a state property:

$$e_3 - e_1 = \int_{T_1}^{T_3} c_v(T) dT + a \left(\frac{1}{v_1} - \frac{1}{v_3} \right) \quad (3.132)$$

Now

$$c_v = 350 + 0.2(T - 300) = 290 + \frac{1}{5}T \quad (3.133)$$

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so

$$e_3 - e_1 = \int_{T_1}^{T_3} \left(290 + \frac{1}{5}T \right) dT + a \left(\frac{1}{v_1} - \frac{1}{v_3} \right) \quad (3.134)$$

$$= 290 (T_3 - T_1) + \frac{1}{10} (T_3^2 - T_1^2) + a \left(\frac{1}{v_1} - \frac{1}{v_3} \right) \quad (3.135)$$

$$290 (1,000 - 300) + \frac{1}{10} (1,000^2 - 300^2) + 150 \left(\frac{1}{0.598} - \frac{1}{0.0585} \right) \quad (3.136)$$

$$= 203,000 + 91,000 - 2,313 \quad (3.137)$$

$$= 291,687 \text{ J/kg} = 292 \text{ kJ/kg} \quad (3.138)$$

Now from the first law

$$e_3 - e_1 = q_{13} - w_{13} \quad (3.139)$$

$$q_{13} = e_3 - e_1 + w_{13} \quad (3.140)$$

$$q_{13} = 292 - 138 \quad (3.141)$$

$$q_{13} = 154 \text{ kJ/kg} \quad (3.142)$$

The heat transfer is positive as heat was added to the system.

Now find the entropy change. Manipulate the Gibbs equation:

$$T ds = de + P dv \quad (3.143)$$

$$ds = \frac{1}{T} de + \frac{P}{T} dv \quad (3.144)$$

$$ds = \frac{1}{T} \left(c_v(T) dT + \frac{a}{v^2} dv \right) + \frac{P}{T} dv \quad (3.145)$$

$$ds = \frac{1}{T} \left(c_v(T) dT + \frac{a}{v^2} dv \right) + \frac{1}{T} \left(\frac{RT}{v-b} - \frac{a}{v^2} \right) dv \quad (3.146)$$

$$ds = \frac{c_v(T)}{T} dT + \frac{R}{v-b} dv \quad (3.147)$$

$$s_3 - s_1 = \int_{T_1}^{T_3} \frac{c_v(T)}{T} dT + R \ln \frac{v_3 - b}{v_1 - b} \quad (3.148)$$

$$= \int_{300}^{1,000} \left(\frac{290}{T} + \frac{1}{5} \right) dT + R \ln \frac{v_3 - b}{v_1 - b} \quad (3.149)$$

$$= 290 \ln \frac{1,000}{300} + \frac{1}{5} (1,000 - 300) + 200 \ln \frac{0.0585 - 0.001}{0.598 - 0.001} \quad (3.150)$$

$$= 349 + 140 - 468 \quad (3.151)$$

$$= 21 \frac{\text{J}}{\text{kg K}} = 0.021 \frac{\text{kJ}}{\text{kg K}} \quad (3.152)$$

Is the second law satisfied for each portion of the process?

First look at 1 → 2

$$e_2 - e_1 = q_{12} - w_{12} \quad (3.153)$$

$$q_{12} = e_2 - e_1 + w_{12} \quad (3.154)$$

$$q_{12} = \left(\int_{T_1}^{T_2} c_v(T) dT + a \left(\frac{1}{v_1} - \frac{1}{v_2} \right) \right) + \left(RT_1 \ln \left(\frac{v_2 - b}{v_1 - b} \right) + a \left(\frac{1}{v_2} - \frac{1}{v_1} \right) \right) \quad (3.155)$$

$$(3.156)$$

Since $T_1 = T_2$ and canceling the terms in a we get

$$q_{12} = RT_1 \ln \left(\frac{v_2 - b}{v_1 - b} \right) = 200 \times 300 \ln \left(\frac{0.0585 - 0.001}{0.598 - 0.001} \right) = -140,408 \frac{J}{kg} \quad (3.157)$$

Since isothermal

$$s_2 - s_1 = R \ln \left(\frac{v_2 - b}{v_1 - b} \right) \quad (3.158)$$

$$= 200 \ln \left(\frac{0.0585 - 0.001}{0.598 - 0.001} \right) \quad (3.159)$$

$$= -468.0 \frac{J}{kg K} \quad (3.160)$$

Entropy *drops* because heat was transferred *out* of the system.

Check the second law. Note that in this portion of the process in which the heat is transferred out of the system, that the surroundings must have $T_{surr} \leq 300 K$. For this portion of the process let us take $T_{surr} = 300 K$.

$$s_2 - s_1 \geq \frac{q_{12}}{T} \quad (3.161)$$

$$-468.0 \frac{J}{kg K} \geq \frac{-140,408 \frac{J}{kg}}{300 K} \quad (3.162)$$

$$-468.0 \frac{J}{kg K} \geq -468.0 \frac{J}{kg K} \quad \text{ok} \quad (3.163)$$

Next look at $2 \rightarrow 3$

$$q_{23} = e_3 - e_2 + w_{23} \quad (3.164)$$

$$q_{23} = \left(\int_{T_2}^{T_3} c_v(T) dT + a \left(\frac{1}{v_2} - \frac{1}{v_3} \right) \right) + \left(\int_{v_2}^{v_3} P dv \right) \quad (3.165)$$

$$\text{since isochoric} \quad q_{23} = \int_{T_2}^{T_3} c_v(T) dT \quad (3.166)$$

$$= \int_{300}^{1000} \left(290 + \frac{T}{5} \right) dT = 294,000 \frac{J}{K} \quad (3.167)$$

Now look at the entropy change for the isochoric process:

$$s_3 - s_2 = \int_{T_2}^{T_3} \frac{c_v(T)}{T} dT \quad (3.168)$$

$$= \int_{T_2}^{T_3} \left(\frac{290}{T} + \frac{1}{5} \right) dT \quad (3.169)$$

$$= 290 \ln \frac{1,000}{300} + \frac{1}{5} (1,000 - 300) = 489 \frac{J}{kg K} \quad (3.170)$$

Entropy *rises* because heat transferred *into* system.

In order to transfer heat into the system we must have a different thermal reservoir. This one must have $T_{surr} \geq 1000 K$. Assume here that the heat transfer was from a reservoir held at $1,000 K$ to

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assess the influence of the second law.

$$s_3 - s_2 \geq \frac{q_{23}}{T} \quad (3.171)$$

$$489 \frac{J}{kg K} \geq \frac{294,000 \frac{J}{kg}}{1,000 K} \quad (3.172)$$

$$489 \frac{J}{kg K} \geq 294 \frac{J}{kg K} \quad \text{ok} \quad (3.173)$$

3.4 Canonical Equations of State

If we have a single equation of state in a special *canonical* form, we can form both thermal and caloric equations. Since

$$de = Tds - Pdv \quad (3.174)$$

$$dh = Tds + vdP \quad (3.175)$$

it is suggested that the form

$$e = e(s, v) \quad (3.176)$$

$$h = h(s, P) \quad (3.177)$$

is useful.

Example 3.7

Canonical Form

If

$$h(s, P) = Kc_p P^{R/c_p} \exp\left(\frac{s}{c_p}\right) + (h_o - c_p T_o) \quad (3.178)$$

derive both thermal and caloric state equations $P(v, T)$ and $e(v, T)$.

Now for our material

$$\left. \frac{\partial h}{\partial s} \right|_P = K P^{R/c_p} \exp\left(\frac{s}{c_p}\right) \quad (3.179)$$

$$\left. \frac{\partial h}{\partial P} \right|_s = K R P^{R/c_p - 1} \exp\left(\frac{s}{c_p}\right) \quad (3.180)$$

Now since

$$\left. \frac{\partial h}{\partial s} \right|_P = T \quad (3.181)$$

$$\left. \frac{\partial h}{\partial P} \right|_s = v \quad (3.182)$$

we have

$$T = KP^{R/c_p} \exp\left(\frac{s}{c_p}\right) \quad (3.183)$$

$$v = KR P^{R/c_p-1} \exp\left(\frac{s}{c_p}\right) \quad (3.184)$$

Dividing one by the other gives

$$\frac{T}{v} = \frac{P}{R} \quad (3.185)$$

$$P = \frac{RT}{v} \quad (3.186)$$

Substituting our expression for T into our canonical equation for h we also get

$$h = c_p T + (h_o - c_p T_o) \quad (3.187)$$

$$h = c_p(T - T_o) + h_o \quad (3.188)$$

which is useful in itself. Substituting in for T and T_o

$$h = c_p \left(\frac{Pv}{R} - \frac{P_o v_o}{R} \right) + h_o \quad (3.189)$$

Using $h \equiv e + Pv$ we get

$$e + Pv = c_p \left(\frac{Pv}{R} - \frac{P_o v_o}{R} \right) + e_o + P_o v_o \quad (3.190)$$

so

$$e = \left(\frac{c_p}{R} - 1 \right) Pv - \left(\frac{c_p}{R} - 1 \right) P_o v_o + e_o \quad (3.191)$$

$$e = \left(\frac{c_p}{R} - 1 \right) (Pv - P_o v_o) + e_o \quad (3.192)$$

$$e = \left(\frac{c_p}{R} - 1 \right) (RT - RT_o) + e_o \quad (3.193)$$

$$e = (c_p - R)(T - T_o) + e_o \quad (3.194)$$

$$e = [c_p - (c_p - c_v)](T - T_o) + e_o \quad (3.195)$$

$$e = c_v(T - T_o) + e_o \quad (3.196)$$

So **one** canonical equation gives us all the information we need! Oftentimes, it is difficult to do a single experiment to get the canonical form.

Exercise: For a calorically perfect ideal gas, write the Helmholtz free energy and Gibbs free energy in canonical form, i.e. what is $a(T, v)$, $g(P, T)$?

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3.5 Isentropic Relations

Of particular importance in thermodynamics in general and compressible flow in particular are relations that describe an isentropic process, $s = \text{constant}$. Recall the second law.

$$ds \geq \frac{dq}{T} \quad (3.197)$$

If the process is **reversible**,

$$ds = \frac{dq}{T} \quad (3.198)$$

If the process is **adiabatic**

$$dq \equiv 0 \quad \text{so} \quad ds = 0 \quad (3.199)$$

So an isentropic process is both adiabatic and reversible. We know from the first law written in terms of entropy that this implies that

$$\mathbf{q} \equiv 0 \quad (3.200)$$

$$\boldsymbol{\tau} \equiv 0 \quad (3.201)$$

In this case the Gibbs relation and the first law reduce to the same expression:

$$de = -Pdv \quad (3.202)$$

That is the energy change is all due to reversible pressure volume work.

We would like to develop an expression between two variables for an isentropic process.

With knowledge of $P(T, v)$

- form $e(T, v)$
- eliminate T to form $e(P, v)$
- take derivative and substitute into Gibbs/First Law

$$\left. \frac{\partial e}{\partial P} \right|_v dP + \left. \frac{\partial e}{\partial v} \right|_P dv = -Pdv \quad (3.203)$$

$$\left. \frac{\partial e}{\partial P} \right|_v dP + \left(\left. \frac{\partial e}{\partial v} \right|_P + P \right) dv = 0 \quad (3.204)$$

Integration of this equation gives a relationship between P and v .

Example 3.8

Calorically Perfect Ideal Gas

Find the relationship for a calorically perfect ideal gas which undergoes an isentropic process.

Ideal Gas:

$$Pv = RT \quad (3.205)$$

Calorically Perfect:

$$e = c_v T + e_o \quad (3.206)$$

Thus

$$e = c_v \frac{Pv}{R} + e_o = \frac{c_v}{c_P - c_v} Pv + e_o = \frac{1}{\gamma - 1} Pv + e_o \quad (3.207)$$

Thus the necessary derivatives are

$$\left. \frac{\partial e}{\partial P} \right|_v = \frac{1}{\gamma - 1} v \quad (3.208)$$

$$\left. \frac{\partial e}{\partial v} \right|_P = \frac{1}{\gamma - 1} P \quad (3.209)$$

so substituting into our developed relationship gives

$$\frac{1}{\gamma - 1} v dP + \left(\frac{1}{\gamma - 1} P + P \right) dv = 0 \quad (3.210)$$

$$v dP + \gamma P dv = 0 \quad (3.211)$$

$$\frac{dP}{P} = -\gamma \frac{dv}{v} \quad (3.212)$$

$$\ln \frac{P}{P_o} = -\gamma \ln \frac{v}{v_o} \quad (3.213)$$

$$\ln \frac{P}{P_o} = \ln \left(\frac{v_o}{v} \right)^\gamma \quad (3.214)$$

$$\frac{P}{P_o} = \left(\frac{v_o}{v} \right)^\gamma \quad (3.215)$$

$$Pv^\gamma = P_o v_o^\gamma = \text{constant} \quad (3.216)$$

also using the thermal state equation

$$\frac{P}{P_o} = \frac{\frac{RT}{v}}{\frac{RT_o}{v_o}} = \frac{T}{T_o} \frac{v_o}{v} = \left(\frac{v_o}{v} \right)^\gamma \quad (3.217)$$

$$\frac{T}{T_o} = \left(\frac{v_o}{v} \right)^{\gamma-1} = \left(\frac{P}{P_o} \right)^{\frac{\gamma-1}{\gamma}} \quad (3.218)$$

Find the work in a process from v_1 to v_2

$$w_{12} = \int_2^1 P dv \quad (3.219)$$

$$= P_o v_o^\gamma \int_{v_1}^{v_2} \frac{dv}{v^\gamma} \quad (3.220)$$

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$$= P_o v_o^\gamma \left[\frac{v^{1-\gamma}}{1-\gamma} \right]_{v_1}^{v_2} \tag{3.221}$$

$$= \frac{P_o v_o^\gamma}{1-\gamma} (v_2^{1-\gamma} - v_1^{1-\gamma}) \tag{3.222}$$

$$= \frac{P_2 v_2 - P_1 v_1}{1-\gamma} \tag{3.223}$$

Also

$$de = dq - dw = 0 - dw \quad \text{so} \tag{3.224}$$

$$e_2 - e_1 = \frac{P_2 v_2 - P_1 v_1}{\gamma - 1} \tag{3.225}$$

Figure 3.4 gives a sketch for the calorically perfect ideal gas undergoing an isentropic expansion in various planes.

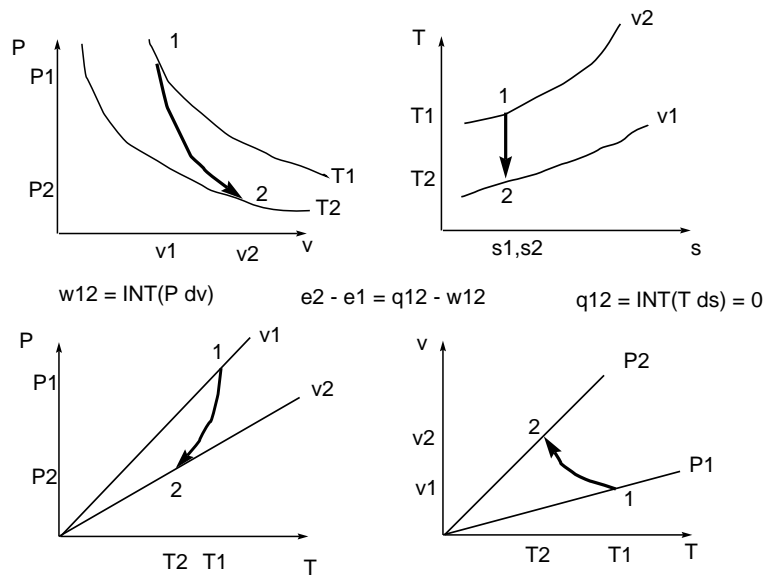


Figure 3.4: Sketch of isentropic process

Example 3.9

Virial Gas

Find the relationship between P and v for a virial gas with constant c_v which undergoes an isentropic process.

Virial Gas:

$$P = \frac{RT}{v - b} \tag{3.226}$$

This is van der Waals with $a = 0$ and c_v constant so:

$$e = c_v T + e_o \quad (3.227)$$

Thus

$$e = c_v \frac{P(v-b)}{R} + e_o \quad (3.228)$$

Thus the necessary derivatives are

$$\left. \frac{\partial e}{\partial P} \right|_v = \frac{c_v}{R} (v-b) \quad (3.229)$$

$$\left. \frac{\partial e}{\partial v} \right|_P = \frac{c_v}{R} P \quad (3.230)$$

so substituting into our developed relationship gives

$$\frac{c_v}{R} (v-b) dP + \left(\frac{c_v}{R} P + P \right) dv = 0 \quad (3.231)$$

$$(v-b) dP + \left(1 + \frac{R}{c_v} \right) P dv = 0 \quad (3.232)$$

$$\text{with } \hat{\gamma} \equiv 1 + \frac{R}{c_v} \quad (3.233)$$

$$\frac{dP}{dv} + \frac{\hat{\gamma}}{v-b} P = 0 \quad (3.234)$$

$$\left(\exp \int \frac{\hat{\gamma}}{v-b} dv \right) \frac{dP}{dv} + \left(\exp \int \frac{\hat{\gamma}}{v-b} dv \right) \frac{\hat{\gamma}}{v-b} P = 0 \quad (3.235)$$

$$\left(\exp \left(\ln (v-b)^{\hat{\gamma}} \right) \right) \frac{dP}{dv} + \left(\exp \left(\ln (v-b)^{\hat{\gamma}} \right) \right) \frac{\hat{\gamma}}{v-b} P = 0 \quad (3.236)$$

$$(v-b)^{\hat{\gamma}} \frac{dP}{dv} + (v-b)^{\hat{\gamma}} \frac{\hat{\gamma}}{v-b} P = 0 \quad (3.237)$$

$$\frac{d}{dv} \left((v-b)^{\hat{\gamma}} P \right) = 0 \quad (3.238)$$

$$(v-b)^{\hat{\gamma}} P = (v_o - b)^{\hat{\gamma}} P_o \quad (3.239)$$

$$\frac{P}{P_o} = \left(\frac{v_o - b}{v-b} \right)^{\hat{\gamma}} \quad (3.240)$$

Exercise: Find the relationship between T and v for a virial gas in an isentropic process.

Exercise: Find an expression for the work done by a van der Waals gas in an isentropic process.

Exercise: A virial gas, $m = 3 \text{ kg}$ with $R = 290 \frac{\text{J}}{\text{kgK}}$, $b = 0.002 \frac{\text{m}^3}{\text{kg}}$ with constant specific heat $c_v = 0.700 \frac{\text{kJ}}{\text{kgK}}$ is initially at $P = 1.2 \text{ bar}$ and $T = 320 \text{ K}$. It undergoes a two step process: $1 \rightarrow 2$ is an isochoric compression to 500 kPa ; $2 \rightarrow 3$ is an isentropic expansion to 300 kPa . Find the total work W_{13} in units of J , the total heat transfer Q_{13} in units of J , and the change in entropy $S_3 - S_1$ in units of J/K . Include a sketch, roughly to scale, of the total process in the $P - v$ and $T - s$ planes.