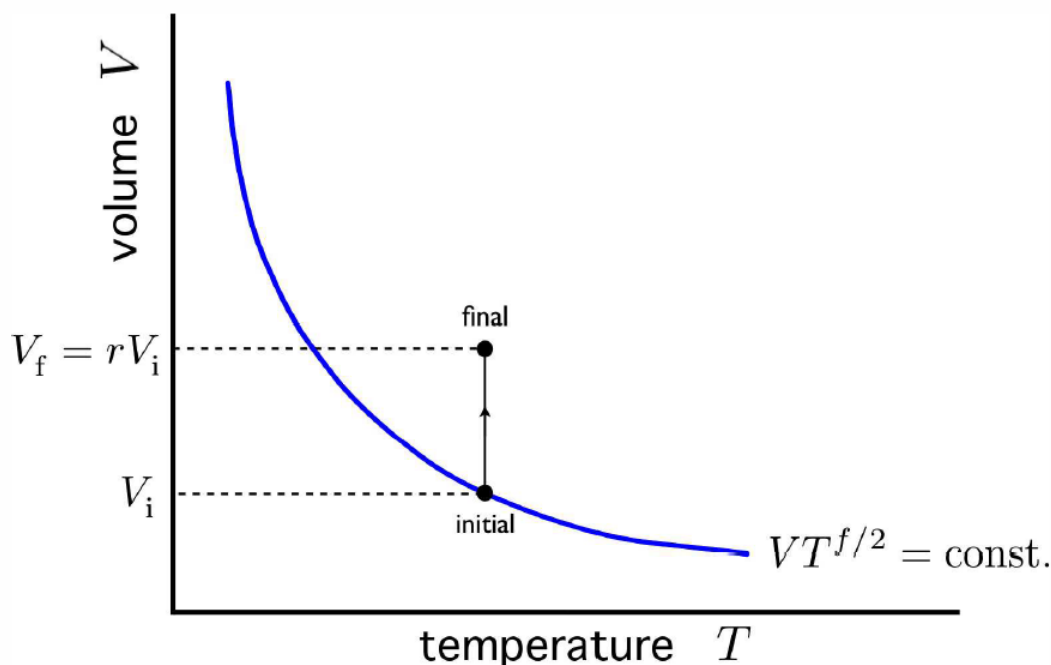


2.10: Applications of Thermodynamics

A discussion of various useful mathematical relations among partial derivatives may be found in the appendix in §17. Some facility with the differential multivariable calculus is extremely useful in the analysis of thermodynamics problems.

Adiabatic free expansion revisited

Consider once again the adiabatic free expansion of a gas from initial volume V_i to final volume $V_f = rV_i$. Since the system is not in equilibrium during the free expansion process, the initial and final states do not lie along an adiabat, they do not have the same entropy. Rather, as we found, from $Q = W = 0$, we have that $E_i = E_f$, which means they have the same *energy*, and, in the case of an ideal gas, the same temperature (assuming N is constant). Thus, the initial and final states lie along an *isotherm*. The situation is depicted in Fig. [AFEgraph]. Now let us compute the change in entropy $\Delta S = S_f - S_i$ by integrating along this isotherm. Note that the actual dynamics are *irreversible* and *do not* quasistatically follow any continuous thermodynamic path. However, we can use what is a fictitious thermodynamic path as a means of comparing S in the initial and final states.



[AFEgraph] Adiabatic free expansion via a thermal path. The initial and final states do not lie along an adiabat! Rather, for an ideal gas, the initial and final states lie along an isotherm.

We have

$$\Delta S = S_f - S_i = \int_{V_i}^{V_f} dV \left(\frac{\partial S}{\partial V} \right)_{T,N}. \quad (2.10.1)$$

But from a Maxwell equation deriving from F , we have

$$\left(\frac{\partial S}{\partial V} \right)_{T,N} = \left(\frac{\partial p}{\partial T} \right)_{V,N}, \quad (2.10.2)$$

hence

$$\Delta S = \int_{V_i}^{V_f} dV \left(\frac{\partial p}{\partial T} \right)_{V,N}. \quad (2.10.3)$$

For an ideal gas, we can use the equation of state $pV = Nk_B T$ to obtain

$$\left(\frac{\partial p}{\partial T}\right)_{V,N} = \frac{Nk_B}{V}. \quad (2.10.4)$$

The integral can now be computed:

$$\Delta S = \int_{V_i}^{rV_i} dV \frac{Nk_B}{V} = Nk_B \ln r, \quad (2.10.5)$$

as we found before, in Equation [AFEdS] What is different about this derivation? Previously, we derived the entropy change from the explicit formula for $S(E, V, N)$. Here, we did not need to know this function. The Maxwell relation allowed us to compute the entropy change using only the equation of state.

Energy and volume

We saw how $E(T, V, N) = \frac{1}{2} f N k_B T$ for an ideal gas, independent of the volume. In general we should have

$$E(T, V, N) = N \phi\left(T, \frac{V}{N}\right). \quad (2.10.6)$$

For the ideal gas, $\phi\left(T, \frac{V}{N}\right) = \frac{1}{2} f k_B T$ is a function of T alone and is independent on the other intensive quantity V/N . How does energy vary with volume? At fixed temperature and particle number, we have, from $E = F + TS$,

$$\left(\frac{\partial E}{\partial V}\right)_{T,N} = \left(\frac{\partial F}{\partial V}\right)_{T,N} + T \left(\frac{\partial S}{\partial V}\right)_{T,N} = -p + T \left(\frac{\partial p}{\partial T}\right)_{V,N}, \quad (2.10.7)$$

where we have used the Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial p}{\partial T}\right)_{V,N}$, derived from the mixed second derivative $\frac{\partial^2 F}{\partial T \partial V}$. Another way to derive this result is as follows. Write $dE = T dS - p dV + \mu dN$ and then express dS in terms of dT , dV , and dN , resulting in

$$dE = T \left(\frac{\partial S}{\partial T}\right)_{V,N} dT + \left[T \left(\frac{\partial S}{\partial V}\right)_{T,N} - p\right] dV - \left[T \left(\frac{\partial \mu}{\partial T}\right)_{V,N} + \mu\right] dN. \quad (2.10.8)$$

Now read off $\left(\frac{\partial E}{\partial V}\right)_{T,N}$ and use the same Maxwell relation as before to recover Equation [pEVTN]. Applying this result to the ideal gas law $pV = Nk_B T$ results in the vanishing of the RHS, hence for any substance obeying the ideal gas law we must have

$$E(T, V, N) = \nu \varepsilon(T) = N \varepsilon(T) / N_A. \quad (2.10.9)$$

van der Waals equation of state

It is clear that the same conclusion follows for any equation of state of the form $p(T, V, N) = T \cdot f(V/N)$, where $f(V/N)$ is an arbitrary function of its argument: the ideal gas law remains valid¹¹. This is not true, however, for the van der Waals equation of state,

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT, \quad (2.10.10)$$

where $v = N_A V / N$ is the molar volume. We then find (always assuming constant N),

$$\left(\frac{\partial E}{\partial V}\right)_T = \left(\frac{\partial \varepsilon}{\partial v}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p = \frac{a}{v^2}, \quad (2.10.11)$$

where $E(T, V, N) \equiv \nu \varepsilon(T, v)$. We can integrate this to obtain

$$\varepsilon(T, v) = \omega(T) - \frac{a}{v}, \quad (2.10.12)$$

where $\omega(T)$ is arbitrary. From Equation [cveqn], we immediately have

$$c_V = \left(\frac{\partial \varepsilon}{\partial T}\right)_v = \omega'(T). \quad (2.10.13)$$

[vdwab] Van der Waals parameters for some common gases. (Source: Wikipedia.)

| gas | $a \left(\frac{\text{L}^2 \cdot \text{bar}}{\text{mol}^2} \right)$ | $b \left(\frac{\text{L}}{\text{mol}} \right)$ | p_c (bar) | T_c (K) | v_c (L/mol) |
|----------------|---|--|-------------|-----------|---------------|
| Acetone | 14.09 | 0.0994 | 52.82 | 505.1 | 0.2982 |
| Argon | 1.363 | 0.03219 | 48.72 | 150.9 | 0.0966 |
| Carbon dioxide | 3.640 | 0.04267 | 7404 | 304.0 | 0.1280 |
| Ethanol | 12.18 | 0.08407 | 63.83 | 516.3 | 0.2522 |
| Freon | 10.78 | 0.0998 | 40.09 | 384.9 | 0.2994 |
| Helium | 0.03457 | 0.0237 | 2.279 | 5.198 | 0.0711 |
| Hydrogen | 0.2476 | 0.02661 | 12.95 | 33.16 | 0.0798 |
| Mercury | 8.200 | 0.01696 | 1055 | 1723 | 0.0509 |
| Methane | 2.283 | 0.04278 | 46.20 | 190.2 | 0.1283 |
| Nitrogen | 1.408 | 0.03913 | 34.06 | 128.2 | 0.1174 |
| Oxygen | 1.378 | 0.03183 | 50.37 | 154.3 | 0.0955 |
| Water | 5.536 | 0.03049 | 220.6 | 647.0 | 0.0915 |

What about c_p ? This requires a bit of work. We start with Equation [cpeqn],

$$c_p = \left(\frac{\partial \varepsilon}{\partial T} \right)_p + p \left(\frac{\partial v}{\partial T} \right)_p$$

$$= \omega'(T) + \left(p + \frac{a}{v^2} \right) \left(\frac{\partial v}{\partial T} \right)_p$$

We next take the differential of the equation of state (at constant N):

$$R dT = \left(p + \frac{a}{v^2} \right) dv + (v - b) \left(dp - \frac{2a}{v^3} dv \right)$$

$$= \left(p - \frac{a}{v^2} + \frac{2ab}{v^3} \right) dv + (v - b) dp.$$

We can now read off the result for the volume expansion coefficient,

$$\alpha_p = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p = \frac{1}{v} \cdot \frac{R}{p - \frac{a}{v^2} + \frac{2ab}{v^3}}. \quad (2.10.14)$$

We now have for c_p ,

$$c_p = \omega'(T) + \frac{\left(p + \frac{a}{v^2} \right) R}{p - \frac{a}{v^2} + \frac{2ab}{v^3}}$$

$$= \omega'(T) + \frac{R^2 T v^3}{R T v^3 - 2a(v - b)^2}.$$

where $v = V N_A / N$ is the molar volume.

To fix $\omega(T)$, we consider the $v \rightarrow \infty$ limit, where the density of the gas vanishes. In this limit, the gas must be ideal, hence Equation [EVT] says that $\omega(T) = \frac{1}{2} f R T$. Therefore $c_v(T, v) = \frac{1}{2} f R$, just as in the case of an ideal gas. However, rather than $c_p = c_v + R$, which holds for ideal gases, $c_p(T, v)$ is given by Equation [cpvdw]. Thus,

$$\begin{aligned} c_{V\text{ssr}\{\text{VDW}\}} &= \frac{1}{2} f R \\ c_{p\text{ssr}\{\text{VDW}\}} &= \frac{1}{2} f R + \frac{R^2 T v^3}{R T v^3 - 2a(v - b)^2} \end{aligned}$$

Note that $c_p(a \rightarrow 0) = c_V + R$, which is the ideal gas result.

As we shall see in chapter 7, the van der Waals system is unstable throughout a region of parameters, where it undergoes *phase separation* between high density (liquid) and low density (gas) phases. The above results are valid only in the stable regions of the phase diagram.

Thermodynamic response functions

Consider the entropy S expressed as a function of T , V , and N :

$$dS = \left(\frac{\partial S}{\partial T} \right)_{V,N} dT + \left(\frac{\partial S}{\partial V} \right)_{T,N} dV + \left(\frac{\partial S}{\partial N} \right)_{T,V} dN. \quad (2.10.15)$$

Dividing by dT , multiplying by T , and assuming $dN = 0$ throughout, we have

$$C_p - C_V = T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p. \quad (2.10.16)$$

Appealing to a Maxwell relation derived from $F(T, V, N)$, and then appealing to Equation [boxtwob], we have

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V = - \left(\frac{\partial p}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p. \quad (2.10.17)$$

This allows us to write

$$C_p - C_V = -T \left(\frac{\partial p}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_p^2. \quad (2.10.18)$$

We define the *response functions*,

$$\text{isothermal compressibility: } \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T = -\frac{1}{V} \frac{\partial^2 G}{\partial p^2}$$

$$\text{adiabatic compressibility: } \kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_S = -\frac{1}{V} \frac{\partial^2 \mathcal{H}}{\partial p^2}$$

$$\text{thermal expansivity: } \alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p.$$

Thus,

$$C_p - C_V = V \frac{T \alpha_p^2}{\kappa_T}, \quad (2.10.19)$$

or, in terms of intensive quantities,

$$c_p - c_V = \frac{v T \alpha_p^2}{\kappa_T}, \quad (2.10.20)$$

where, as always, $v = V N_A / N$ is the molar volume.

This above relation generalizes to any conjugate force-displacement pair $(-p, V) \rightarrow (y, X)$:

$$\begin{aligned} C_y - C_X &= -T \left(\frac{\partial y}{\partial T} \right)_X \left(\frac{\partial X}{\partial T} \right)_y \\ &= T \left(\frac{\partial y}{\partial X} \right)_T \left(\frac{\partial X}{\partial T} \right)_y^2. \end{aligned}$$

For example, we could have $(y, X) = (H^\alpha, M^\alpha)$.

A similar relationship can be derived between the compressibilities κ_T and κ_S . We then clearly must start with the volume, writing

$$dV = \left(\frac{\partial V}{\partial p} \right)_{S,N} dp + \left(\frac{\partial V}{\partial S} \right)_{p,N} dS + \left(\frac{\partial V}{\partial N} \right)_{S,p} dN. \quad (2.10.21)$$

Dividing by dp , multiplying by $-V^{-1}$, and keeping N constant, we have

$$\kappa_T - \kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial S} \right)_p \left(\frac{\partial S}{\partial p} \right)_T. \quad (2.10.22)$$

Again we appeal to a Maxwell relation, writing

$$\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p, \quad (2.10.23)$$

and after invoking the chain rule,

$$\left(\frac{\partial V}{\partial S} \right)_p = \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial T}{\partial S} \right)_p = \frac{T}{C_p} \left(\frac{\partial V}{\partial T} \right)_p, \quad (2.10.24)$$

we obtain

$$\kappa_T - \kappa_S = \frac{v T \alpha_p^2}{c_p}. \quad (2.10.25)$$

Comparing eqns. [inta] and [intb], we find

$$(c_p - c_V) \kappa_T = (\kappa_T - \kappa_S) c_p = v T \alpha_p^2. \quad (2.10.26)$$

This result entails

$$\frac{c_p}{c_V} = \frac{\kappa_T}{\kappa_S}. \quad (2.10.27)$$

The corresponding result for magnetic systems is

$$(c_H - c_M) \chi_T = (\chi_T - \chi_S) c_H = T \left(\frac{\partial m}{\partial T} \right)_H^2, \quad (2.10.28)$$

where $m = M/\nu$ is the magnetization per mole of substance, and

$$\text{isothermal susceptibility: } \chi_T = \left(\frac{\partial M}{\partial H} \right)_T = -\frac{1}{\nu} \frac{\partial^2 G}{\partial H^2}$$

$$\text{adiabatic susceptibility: } \chi_S = \left(\frac{\partial M}{\partial H} \right)_S = -\frac{1}{\nu} \frac{\partial^2 \mathcal{H}}{\partial H^2}.$$

Here the enthalpy and Gibbs free energy are

$$\begin{aligned} \mathcal{H} &= E - HM & d\mathcal{H} &= T dS - M dH \\ G &= E - TS - HM & dG &= -S dT - M dH. \end{aligned}$$

Remark: The previous discussion has assumed an isotropic magnetic system where \mathbf{M} and \mathbf{H} are collinear, hence $\mathbf{H} \cdot \mathbf{M} = HM$.

$$\begin{aligned} \chi_T^{\alpha\beta} &= \left(\frac{\partial M^\alpha}{\partial H^\beta} \right)_T = -\frac{1}{\nu} \frac{\partial^2 G}{\partial H^\alpha \partial H^\beta} \\ \chi_S^{\alpha\beta} &= \left(\frac{\partial M^\alpha}{\partial H^\beta} \right)_S = -\frac{1}{\nu} \frac{\partial^2 \mathcal{H}}{\partial H^\alpha \partial H^\beta}. \end{aligned}$$

In this case, the enthalpy and Gibbs free energy are

$$\begin{aligned} \mathcal{H} &= E - \mathbf{H} \cdot \mathbf{M} & d\mathcal{H} &= T dS - \mathbf{M} \cdot d\mathbf{H} \\ G &= E - TS - \mathbf{H} \cdot \mathbf{M} & dG &= -S dT - \mathbf{M} \cdot d\mathbf{H}. \end{aligned}$$

Joule effect: free expansion of a gas

Previously we considered the adiabatic free expansion of an ideal gas. We found that $Q = W = 0$ hence $\Delta E = 0$, which means the process is isothermal, since $E = \nu \varepsilon(T)$ is volume-independent. The entropy changes, however, since $S(E, V, N) = Nk_B \ln(V/N) + \frac{1}{2} f N k_B \ln(E/N) + N s_0$. Thus,

$$S_f = S_i + Nk_B \ln\left(\frac{V_f}{V_i}\right). \quad (2.10.29)$$

What happens if the gas is nonideal?

We integrate along a fictitious thermodynamic path connecting initial and final states, where $dE = 0$ along the path. We have

$$0 = dE = \left(\frac{\partial E}{\partial V}\right)_T dV + \left(\frac{\partial E}{\partial T}\right)_V dT \quad (2.10.30)$$

hence

$$\left(\frac{\partial T}{\partial V}\right)_E = -\frac{(\partial E/\partial V)_T}{(\partial E/\partial T)_V} = -\frac{1}{C_V} \left(\frac{\partial E}{\partial V}\right)_T. \quad (2.10.31)$$

We also have

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - p = T \left(\frac{\partial p}{\partial T}\right)_V - p. \quad (2.10.32)$$

Thus,

$$\left(\frac{\partial T}{\partial V}\right)_E = \frac{1}{C_V} \left[p - T \left(\frac{\partial p}{\partial T}\right)_V \right]. \quad (2.10.33)$$

Note that the term in square brackets vanishes for any system obeying the ideal gas law. For a nonideal gas,

$$\Delta T = \int_{V_i}^{V_f} dV \left(\frac{\partial T}{\partial V}\right)_E, \quad (2.10.34)$$

which is in general nonzero.

Now consider a van der Waals gas, for which

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT. \quad (2.10.35)$$

We then have

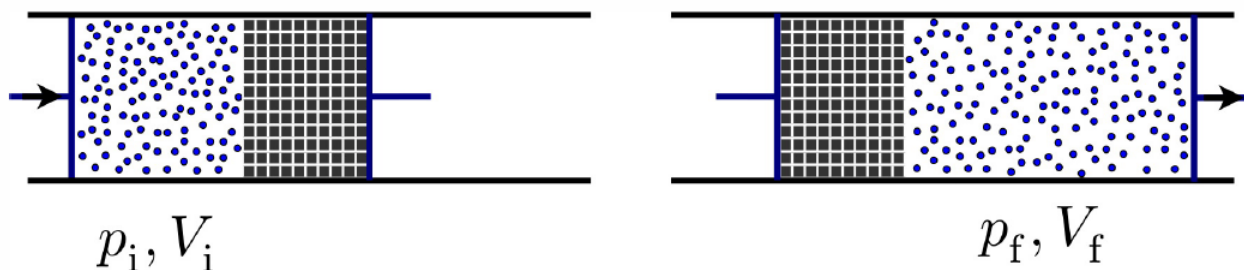
$$p - T \left(\frac{\partial p}{\partial T}\right)_V = -\frac{a}{v^2} = -\frac{a\nu^2}{V^2}. \quad (2.10.36)$$

In §11.3 we concluded that $C_V = \frac{1}{2} f \nu R$ for the van der Waals gas, hence

$$\Delta T = -\frac{2a\nu}{fR} \int_{V_i}^{V_f} \frac{dV}{V^2} = \frac{2a}{fR} \left(\frac{1}{v_f} - \frac{1}{v_i}\right). \quad (2.10.37)$$

Thus, if $V_f > V_i$, we have $T_f < T_i$ and the gas cools upon expansion.

Consider O_2 gas with an initial specific volume of $v_i = 22.4 \text{ L/mol}$, which is the STP value for an ideal gas, freely expanding to a volume $v_f = \infty$ for maximum cooling. According to table [vdwab], $a = 1.378 \text{ L}^2 \cdot \text{bar/mol}^2$, and we have $\Delta T = -2a/fRv_i = -0.296 \text{ K}$, which is a pitifully small amount of cooling. Adiabatic free expansion is a very inefficient way to cool a gas.



[throttle] In a throttle, a gas is pushed through a porous plug separating regions of different pressure. The change in energy is the work done, hence enthalpy is conserved during the throttling process.

Throttling: the Joule-Thompson effect

In a throttle, depicted in Fig. [throttle], a gas is forced through a porous plug which separates regions of different pressures. According to the figure, the work done on a given element of gas is

$$W = \int_0^{V_f} dV p_f - \int_0^{V_i} dV p_i = p_f V_f - p_i V_i. \quad (2.10.38)$$

Now we assume that the system is thermally isolated so that the gas exchanges no heat with its environment, nor with the plug. Then $Q = 0$ so $\Delta E = -W$, and

$$\begin{aligned} E_i + p_i V_i &= E_f + p_f V_f \\ \mathcal{H}_i &= \mathcal{H}_f, \end{aligned}$$

where \mathcal{H} is enthalpy. Thus, the throttling process is *isenthalpic*. We can therefore study it by defining a fictitious thermodynamic path along which $d\mathcal{H} = 0$. The, choosing T and p as state variables,

$$0 = d\mathcal{H} = \left(\frac{\partial \mathcal{H}}{\partial T} \right)_p dT + \left(\frac{\partial \mathcal{H}}{\partial p} \right)_T dp \quad (2.10.39)$$

hence

$$\left(\frac{\partial T}{\partial p} \right)_{\mathcal{H}} = - \frac{(\partial \mathcal{H} / \partial p)_T}{(\partial \mathcal{H} / \partial T)_p}. \quad (2.10.40)$$

The numerator on the RHS is computed by writing $d\mathcal{H} = T dS + V dp$ and then dividing by dp , to obtain

$$\left(\frac{\partial \mathcal{H}}{\partial p} \right)_T = V + T \left(\frac{\partial S}{\partial p} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_p. \quad (2.10.41)$$

The denominator is

$$\begin{aligned} \left(\frac{\partial \mathcal{H}}{\partial T} \right)_p &= \left(\frac{\partial \mathcal{H}}{\partial S} \right)_p \left(\frac{\partial S}{\partial T} \right)_p \\ &= T \left(\frac{\partial S}{\partial T} \right)_p = C_p. \end{aligned}$$

Thus,

$$\begin{aligned} \left(\frac{\partial T}{\partial p} \right)_{\mathcal{H}} &= \frac{1}{C_p} \left[T \left(\frac{\partial v}{\partial T} \right)_p - v \right] \\ &= \frac{v}{C_p} (T \alpha_p - 1), \end{aligned}$$

where $\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$ is the volume expansion coefficient.

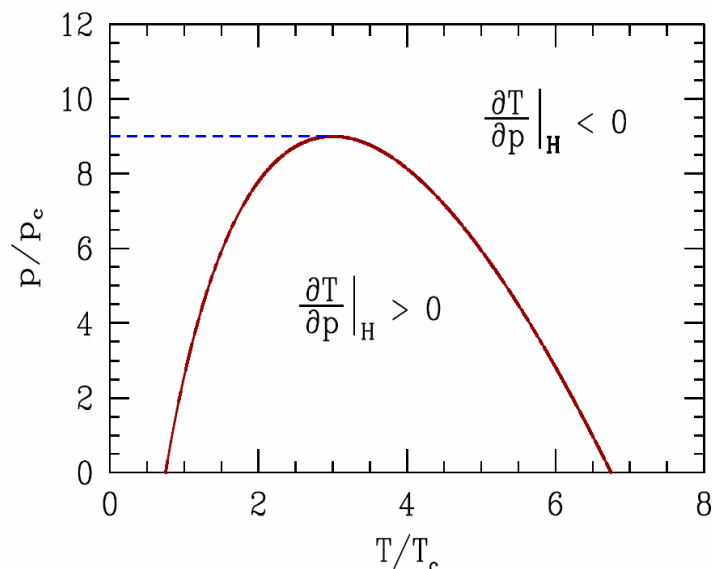
From the van der Waals equation of state, we obtain, from Equation 2.10.14

$$T\alpha_p = \frac{T}{v} \left(\frac{\partial v}{\partial T} \right)_p = \frac{RT/v}{p - \frac{a}{v^2} + \frac{2ab}{v^3}} = \frac{v-b}{v - \frac{2a}{RT} \left(\frac{v-b}{v} \right)^2} . \quad (2.10.42)$$

Assuming $v \gg \frac{a}{RT}, b$, we have

$$\left(\frac{\partial T}{\partial p} \right)_H = \frac{1}{c_p} \left(\frac{2a}{RT} - b \right) . \quad (2.10.43)$$

Thus, for $T > T^* = \frac{2a}{Rb}$, we have $\left(\frac{\partial T}{\partial p} \right)_H < 0$ and the gas heats up upon an isenthalpic pressure decrease. For $T < T^*$, the gas cools under such conditions.



[itvdw] Inversion temperature $T^*(p)$ for the van der Waals gas. Pressure and temperature are given in terms of $p_c = a/27b^2$ and $T_c = 8a/27bR$, respectively.

In fact, there are two inversion temperatures $T_{1,2}^*$ for the van der Waals gas. To see this, we set $T\alpha_p = 1$, which is the criterion for inversion. From Equation 2.10.42 it is easy to derive $\left(\frac{\partial v}{\partial T} \right)_p = \frac{1}{v} \sqrt{\frac{2a}{RT}}$

\. \) We insert this into the van der Waals equation of state to derive a relationship $T = T^*(p)$ at which $T\alpha_p = 1$ holds. After a little work, we find

$$p = -\frac{3RT}{2b} + \sqrt{\frac{8aRT}{b^3}} - \frac{a}{b^2} . \quad (2.10.44)$$

This is a quadratic equation for T , the solution of which is

$$T^*(p) = \frac{2a}{9bR} \left(2 \pm \sqrt{1 - \frac{3b^2p}{a}} \right)^2 . \quad (2.10.45)$$

In Fig. [itvdw] we plot pressure *versus* temperature in scaled units, showing the curve along which $\left(\frac{\partial T}{\partial p} \right)_H = 0$. The volume, pressure, and temperature scales defined are

$$v_c = 3b \quad , \quad p_c = \frac{a}{27b^2} \quad , \quad T_c = \frac{8a}{27bR} . \quad (2.10.46)$$

Values for p_c , T_c , and v_c are provided in table [vdwab]. If we define $v = v/v_c$, $p = p/p_c$, and $T = T/T_c$, then the van der Waals equation of state may be written in dimensionless form:

$$\left(p + \frac{3}{v^2} \right) (3v - 1) = 8T . \quad (2.10.47)$$

In terms of the scaled parameters, the equation for the inversion curve $\left(\frac{\partial T}{\partial p}\right)_H = 0$ becomes

$$p = 9 - 36 \left(1 - \sqrt{\frac{1}{3}T}\right)^2 \iff T = 3 \left(1 \pm \sqrt{1 - \frac{1}{9}p}\right)^2. \quad (2.10.48)$$

Thus, there is no inversion for $p > 9p_c$. We are usually interested in the upper inversion temperature, T_2^* , corresponding to the upper sign in Equation [invtemp]. The maximum inversion temperature occurs for $p = 0$, where $T_{max}^* = \frac{2a}{bR} = \frac{27}{4} T_c$. For H_2 , from the data in table [vdwab], we find $T_{max}^*(H_2) = 224\text{ K}$, which is within 10% of the experimentally measured value of 205 K.

What happens when H_2 gas leaks from a container with $T > T_2^*$? Since $\left(\frac{\partial T}{\partial p}\right)_H < 0$ and $\Delta p < 0$, we have $\Delta T > 0$. The gas warms up, and the heat facilitates the reaction $2H_2 + O_2 \longrightarrow 2H_2O$, which releases energy, and we have a nice explosion.

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