

## 0.1 Ideal Gases

### 0.1.1 Basic stuff

- First law of thermodynamics:

$$\Delta E = Q - W \quad \Rightarrow \quad dE = \delta Q - \delta W \quad (\text{differential form}) \quad .$$

- Equation of state:

$$pV = nRT$$

with  $n = N/N_A$  the number of moles, which is assumed conserved unless explicitly stated otherwise.

- Energy:

$$E = \frac{1}{2}fnRT = \frac{nRT}{\gamma - 1} = \frac{pV}{\gamma - 1}$$

with  $\gamma = 1 + \frac{2}{f}$  and  $f$  is the number of molecular degrees of freedom (translations plus rotations). We then have

$$\begin{pmatrix} f_{\text{mono}} \\ f_{\text{dia}} \\ f_{\text{poly}} \end{pmatrix} = \begin{pmatrix} 3 \\ 5 \\ 6 \end{pmatrix} \quad , \quad \begin{pmatrix} \gamma_{\text{mono}} \\ \gamma_{\text{dia}} \\ \gamma_{\text{poly}} \end{pmatrix} = \begin{pmatrix} 5/3 \\ 7/5 \\ 4/3 \end{pmatrix} \quad .$$

- Heat capacity:

$$C_V = \left( \frac{\partial E}{\partial T} \right)_{V,N} = \frac{1}{2}fnR = \frac{nR}{\gamma - 1} \quad , \quad C_p = C_V + R = \left( \frac{1}{2}f + 1 \right)nR = \frac{nR}{1 - \gamma^{-1}} \quad ,$$

with  $C_p/C_V = \gamma$ . Per mole,  $c_V = \frac{1}{2}fR = R/(\gamma - 1)$  and  $c_p = (1 + \frac{1}{2}f)R = R/(1 - \gamma^{-1})$ .

- Adiabatic equation of state:

$$\delta Q = C_V dT + p dV = 0 \quad \Rightarrow \quad d \log T + (\gamma - 1)d \log V = 0 \quad .$$

Thus,

$$TV^{\gamma-1} = \text{const.} \quad , \quad pV^\gamma = \text{const.} \quad , \quad T^\gamma p^{1-\gamma} = \text{const.} \quad .$$

### 0.1.2 Reversible ideal gas engine cycle components

◇ Isotherms:  $dT = 0$  and  $p(V) = nRT/V$ . Thus

$$W_{12} = \int_{V_1}^{V_2} p dV = nRT \log(V_2/V_1) \quad ,$$

with  $T_1 = T_2 = T$ . Then  $\Delta E_{12} = 0$  and  $Q_{12} = \Delta E_{12} + W_{12} = W_{12}$ .

◊ Isobars:  $dp = 0$ ,

$$W_{12} = \int_{V_1}^{V_2} p dV = p(V_2 - V_1) = nR(T_2 - T_1) \quad ,$$

since  $p_1 = p_2 = p$ . We also have  $\Delta E_{12} = \frac{1}{2}fnR(T_2 - T_1)$  and therefore

$$Q_{12} = \Delta E_{12} + W_{12} = \left(\frac{1}{2}f + 1\right)nR(T_2 - T_1) \quad .$$

◊ Isochores:  $dV = 0$ . Here there is no work because  $p dV = 0$  along the path. Therefore  $W_{12} = 0$ . We then have

$$\Delta E_{12} = Q_{12} = \frac{1}{2}fnR(T_2 - T_1) \quad .$$

◊ Adiabats:  $\dot{d}Q = T dS = 0$ . We can use  $pV^\gamma = p_1V_1^\gamma = p_2V_2^\gamma$  to write

$$W_{12} = \int_{V_1}^{V_2} p dV = p_1V_1^\gamma \int_{V_1}^{V_2} dV V^{-\gamma} = \frac{p_1V_1 - p_2V_2}{\gamma - 1} = \frac{1}{2}f(p_1V_1 - p_2V_2) = \frac{1}{2}fnR(T_1 - T_2) \quad .$$

But there is an easier way! Since  $Q_{12} = 0$  we have  $W_{12} = -\Delta E_{12} = \frac{1}{2}fnR(T_1 - T_2)$ .

◊ General  $p(V)$ : In this case we have to bite the bullet and compute

$$W_{12} = \int_{V_1}^{V_2} p(V) dV \quad .$$

The energy change is  $\Delta E_{12} = \frac{1}{2}fnR(T_2 - T_1) = \frac{1}{2}f(p_2V_2 - p_1V_1)$  and  $Q_{12} = \Delta E_{12} + W_{12}$ .

## 0.2 Maxwell Relations

For a general function  $\Phi(u_1, u_2, \dots, u_n)$ , if the function itself class  $C^2$  or smoother (meaning all second derivatives exist and are continuous), then

$$\frac{\partial^2 \Phi}{\partial u_i \partial u_j} = \frac{\partial}{\partial u_i} \left( \frac{\partial \Phi}{\partial u_j} \right) = \frac{\partial}{\partial u_j} \left( \frac{\partial \Phi}{\partial u_i} \right) \quad .$$

Let us write

$$d\Phi = R_1 du_1 + R_2 du_2 + \dots + R_n du_n \quad ,$$

with  $R_j \equiv \partial\Phi/\partial u_j$ , where the derivative is computed holding all  $u_i$  for  $u \neq j$  constant. Then the equality of the mixed second partial derivatives is equivalent to the conditions

$$\left( \frac{\partial R_i}{\partial u_j} \right)_{u_{k(\neq j)}} = \left( \frac{\partial R_j}{\partial u_i} \right)_{u_{k(\neq i)}} \quad .$$

The Helmholtz free energy  $F = E - TS$ , Gibbs free energy  $E - TS + pV$ , and enthalpy  $H = E + pV$  are Legendre transforms of the energy function. Their respective differentials are given by

$$\begin{aligned} dE &= T dS - p dV + \mu dN \\ dF &= -S dT - p dV + \mu dN \\ dG &= -S dT + V dp + \mu dN \\ dH &= T dS + V dp + \mu dN \end{aligned}$$

These entail the following functional dependences:

$$E = E(S, V, N) \quad , \quad F = F(T, V, N) \quad , \quad G = G(T, p, N) \quad , \quad H = H(S, p, N) \quad .$$

Assuming  $N$  is always fixed, from  $E(S, V, N)$  we have

$$\begin{aligned} \frac{\partial^2 E}{\partial S \partial V} &= \frac{\partial}{\partial S} \left( \frac{\partial E}{\partial V} \right)_{S,N} = \left( \frac{\partial(-p)}{\partial S} \right)_{V,N} \\ &= \frac{\partial}{\partial V} \left( \frac{\partial E}{\partial S} \right)_{V,N} = \left( \frac{\partial T}{\partial V} \right)_{S,N} \Rightarrow \boxed{\left( \frac{\partial p}{\partial S} \right)_{V,N} = - \left( \frac{\partial T}{\partial V} \right)_{S,N}} \end{aligned}$$

From  $F(T, V, N)$  we have

$$\begin{aligned} \frac{\partial^2 F}{\partial T \partial V} &= \frac{\partial}{\partial T} \left( \frac{\partial F}{\partial V} \right)_{T,N} = \left( \frac{\partial(-p)}{\partial T} \right)_{V,N} \\ &= \frac{\partial}{\partial V} \left( \frac{\partial F}{\partial T} \right)_{V,N} = \left( \frac{\partial(-S)}{\partial V} \right)_{T,N} \Rightarrow \boxed{\left( \frac{\partial p}{\partial T} \right)_{V,N} = \left( \frac{\partial S}{\partial V} \right)_{T,N}} \end{aligned}$$

From  $G(T, p, N)$  we have

$$\begin{aligned} \frac{\partial^2 G}{\partial T \partial p} &= \frac{\partial}{\partial T} \left( \frac{\partial G}{\partial p} \right)_{T,N} = \left( \frac{\partial V}{\partial T} \right)_{p,N} \\ &= \frac{\partial}{\partial p} \left( \frac{\partial G}{\partial T} \right)_{p,N} = \left( \frac{\partial(-S)}{\partial p} \right)_{T,N} \Rightarrow \boxed{\left( \frac{\partial V}{\partial T} \right)_{p,N} = - \left( \frac{\partial S}{\partial p} \right)_{T,N}} \end{aligned}$$

and from  $H(S, p, N)$  we have

$$\begin{aligned} \frac{\partial^2 H}{\partial S \partial p} &= \frac{\partial}{\partial S} \left( \frac{\partial H}{\partial p} \right)_{S,N} = \left( \frac{\partial V}{\partial S} \right)_{p,N} \\ &= \frac{\partial}{\partial p} \left( \frac{\partial H}{\partial S} \right)_{p,N} = \left( \frac{\partial T}{\partial p} \right)_{S,N} \Rightarrow \boxed{\left( \frac{\partial V}{\partial S} \right)_{p,N} = \left( \frac{\partial T}{\partial p} \right)_{S,N}} \end{aligned}$$

### 0.3 Nonideal equations of state

#### 0.3.1 van der Waals equation of state

The energy of an ideal gas is given by  $E = \frac{1}{2}fnRT$  and is independent of volume at fixed  $T$  and  $n = N/N_A$  (or  $N$ ). This is not the case for the van der Waals equation of state,

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

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

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

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

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

where  $\omega(T)$  is arbitrary. The molar specific heat at constant volume is then

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

What about  $c_p$ ? This requires a bit of work. We start with  $d\varepsilon = T ds - p dv$ , where  $\varepsilon$ ,  $s$ , and  $v$  are all intensive quantities corresponding to energy, entropy, and volume per mole. Then

$$c_p = T \left(\frac{\partial s}{\partial T}\right)_p = \left(\frac{\partial \varepsilon}{\partial T}\right)_p + p \left(\frac{\partial v}{\partial T}\right)_p = c_V + \left(p + \frac{a}{v^2}\right) \left(\frac{\partial v}{\partial T}\right)_p \quad .$$

We may rewrite the equation of state as

$$p = \frac{RT}{v - b} - \frac{a}{v^2} \quad .$$

Taking the differential of both sides,

$$\begin{aligned} dp &= \left(\frac{\partial p}{\partial T}\right)_v dT + \left(\frac{\partial p}{\partial v}\right)_T dv \\ &= \frac{R}{v - b} dT + \left[-\frac{RT}{(v - b)^2} + \frac{2a}{v^3}\right] dv \quad . \end{aligned}$$

Setting  $dp = 0$ , we may read off

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial p}{\partial T}\right)_v / \left(\frac{\partial p}{\partial v}\right)_T \quad .$$

Putting this all together, we obtain

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{Rv^3(v-b)}{RTv^3 - 2a(v-b)^2} \quad .$$

One immediate result is the following expression for the isobaric thermal expansion coefficient,

$$\alpha_p = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p = \frac{Rv^2(v-b)}{RTv^3 - 2a(v-b)^2} \quad .$$

Another result is the difference  $c_p - c_V$  from eqn. 0.3.1,

$$c_p - c_V = \left(p + \frac{a}{v^2}\right) \left(\frac{\partial v}{\partial T}\right)_p = \frac{R^2Tv^3}{RTv^3 - 2a(v-b)^2} \quad .$$

To fix  $\omega(T)$  and thus  $c_V = \omega'(T)$ , we consider the  $v \rightarrow \infty$  limit, where the density of the gas vanishes. In this limit, the gas must be ideal, hence eqn. 0.3.1 says that  $\omega(T) = \frac{1}{2}fRT$ . Therefore  $c_V(T, v) = \frac{1}{2}fR$ , 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 eqn. 0.3.1. Thus,

$$\begin{aligned} c_V^{\text{VDW}} &= \frac{1}{2}fR \\ c_p^{\text{VDW}} &= \frac{1}{2}fR + \frac{R^2Tv^3}{RTv^3 - 2a(v-b)^2} \quad . \end{aligned}$$

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

It turns out that 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.

### 0.3.2 General equation of state

Suppose we can't isolate any of the state variables in the equation of state as we did when writing  $p = p(T, v)$  above. Rather, let the equation of state take the form  $Z(T, p, v) = 0$ . Setting consecutively  $dv = 0$ ,  $dT = 0$ , and  $dp = 0$ , we then obtain

$$dZ = \left(\frac{\partial Z}{\partial T}\right)_{p,v} dT + \left(\frac{\partial Z}{\partial p}\right)_{T,v} dp + \left(\frac{\partial Z}{\partial v}\right)_{T,p} dv = 0 \quad .$$

We then have

$$\begin{aligned} \left(\frac{\partial T}{\partial p}\right)_v &= - \left(\frac{\partial Z}{\partial p}\right)_{T,v} / \left(\frac{\partial Z}{\partial T}\right)_{p,v} \\ \left(\frac{\partial p}{\partial v}\right)_T &= - \left(\frac{\partial Z}{\partial v}\right)_{T,p} / \left(\frac{\partial Z}{\partial p}\right)_{T,v} \\ \left(\frac{\partial v}{\partial T}\right)_p &= - \left(\frac{\partial Z}{\partial T}\right)_{p,v} / \left(\frac{\partial Z}{\partial v}\right)_{T,p} \quad . \end{aligned}$$