Appendix C

Thermodynamics of the Hugoniot

Using thermodynamics, the jump conditions, and the Hugoniot equation, we can determine if the flow is subsonic or supersonic behind the wave and also the nature of the entropy extremum at the CJ points. Differential equations can be formulated to described the variation of temperature and entropy on the Hugoniot.

C.1   Jouguet's rule

The starting point of this discussion is the variation of entropy on the Hugoniot that was derived from the Fundamental Relation of Thermodynamics and the energy version of the Hugoniot equation 6.19.

$$\left(\frac{\partial s}{\partial v}\right)_{\mathcal{H}} = \frac{\Delta v}{2T}\left[\frac{\Delta P}{\Delta v} - \left(\frac{\partial P}{\partial v}\right)_{\mathcal{H}}\right] \tag{C.1}$$

This expression gives the entropy change in terms of the difference between the slope of the Hugoniot and Rayleigh line. In order to draw conclusions about the flow Mach number, we need to reformulate this in terms of the slope of the isentropes and the Rayleigh line. The relationship of the Hugoniot to the isentropes requires determining the slope of the Hugoniot. This can be accomplished by expanding internal energy $e(P, v)$ as a function of pressure and volume.

$$de = \left(\frac{\partial e}{\partial P}\right)_v dP + \left(\frac{\partial e}{\partial v}\right)_P dv \tag{C.2}$$

Using thermodynamic relationships, we can write the coefficients in terms of the Grüniesen parameter $\mathcal{G}$

$$\mathcal{G} = v\left(\frac{\partial P}{\partial e}\right)_v \tag{C.3}$$

$$= -\frac{v}{T}\left(\frac{\partial T}{\partial v}\right)_s \tag{C.4}$$

$$de = \frac{v}{\mathcal{G}}dP - \left[\frac{v}{\mathcal{G}}\left(\frac{\partial P}{\partial v}\right)_s + P\right]dv \tag{C.5}$$

Equating this to the expression obtained by differentiating the Hugoniot and solving for the slope, we have

$$\left(\frac{\partial P}{\partial v}\right)_{\mathcal{H}} = \frac{\left(\frac{\partial P}{\partial v}\right)_s + \frac{\mathcal{G}}{2v}\Delta P}{1 + \frac{\mathcal{G}}{2v}\Delta v} \tag{C.6}$$

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An independent relationship between the Hugoniot and isentrope slopes can be obtained by expanding $P(v, s)$ on the Hugoniot

$$\left(\frac{\partial P}{\partial v}\right)_{\mathcal{H}} = \left(\frac{\partial P}{\partial v}\right)_{s} + \left(\frac{\partial P}{\partial s}\right)_{v} \left(\frac{\partial s}{\partial v}\right)_{\mathcal{H}} \tag{C.7}$$

This can be simplified by using the thermodynamic relations to read

$$\left(\frac{\partial P}{\partial v}\right)_{\mathcal{H}} = \left(\frac{\partial P}{\partial v}\right)_{s} + \mathcal{G}\frac{T}{v} \left(\frac{\partial s}{\partial v}\right)_{\mathcal{H}} \tag{C.8}$$

Note that the unsubscripted variable v, $\mathcal{G}$, and the slope of the isentrope are to be evaluated at the downstream conditions (2) in this equation. Equation (C.8) indicates how the sign of $\mathcal{G}$ and the rate of change of entropy along the isentrope determines if the slope of the isentrope is larger or smaller than the slope of the Hugoniot. For substances with $\mathcal{G} > 0$, the slope of the Hugoniot will be smaller (larger) than the slope of the isentrope when the entropy derivative $(ds/dv)_{\mathcal{H}} < 0 \ (> 0)$. Shock waves in usual substances (see Menikoff and Plohr, 1989) are compression waves

$$\Delta P > 0 \tag{C.9}$$

and have $\mathcal{G} > 0$ and $(ds/dv)_{\mathcal{H}} < 0$, so that

$$\infty < \left(\frac{\partial P}{\partial v}\right)_{\mathcal{H}} < \left(\frac{\partial P}{\partial v}\right)_{s} < 0 \tag{C.10}$$

and there are no vertical asymptotes (see Hayes, 1960) so that the denominator does not vanish

$$1 + \mathcal{G}\frac{\Delta v}{2v} > 0 \tag{C.11}$$

Combining (C.6) and (C.1) gives

$$\left(\frac{\partial s}{\partial v}\right)_{\mathcal{H}} = \frac{\Delta v}{2T}\left[\frac{\dfrac{\Delta P}{\Delta v} - \left(\dfrac{\partial P}{\partial v}\right)_{s}}{1 + \mathcal{G}\dfrac{\Delta v}{2v}}\right] \tag{C.12}$$

which can also be written as

$$\left(\frac{\partial s}{\partial v}\right)_{\mathcal{H}} = \frac{\Delta v}{2Tv^2}\left[\frac{a^2 - \mathrm{w}^2}{1 + \mathcal{G}\dfrac{\Delta v}{2v}}\right] \tag{C.13}$$

This illuminates a crucial connection between the flow speed (subsonic vs supersonic) downstream of the shock, the Grüniesen parameter, and the variation of entropy along the Hugoniot. The denominator is positive for most substances since the slope of a realistic Hugoniot (C.6) is negative and is a continuous function of the volume. Equating the two expressions for the variation of entropy along the Hugoniot (C.1) and (C.13), we find

$$\frac{\Delta P}{\Delta v} - \left(\frac{\partial P}{\partial v}\right)_{\mathcal{H}} = \frac{1}{v^2}\frac{a^2 - \mathrm{w}^2}{1 + \mathcal{G}\dfrac{\Delta v}{2v}} \tag{C.14}$$

This equation can be applied to the downstream state at any intersection point between the Rayleigh line and the Hugoniot. From the geometry of the Hugoniot and Rayleigh line shown in Fig. 6.4, we conclude that if the denominator of (C.14) is positive, the flow downstream (state 1) of a shock wave is subsonic.

The flow upstream of a shock is supersonic, $w_1 > a_1$, since the isentrope and Hugoniot are tangent at the initial state (C.6) and from the geometry shown in Fig. 6.4, we have

$$\frac{\Delta P}{\Delta v} < \left(\frac{\partial P}{\partial v}\right)_\mathcal{H} = \left(\frac{\partial P}{\partial v}\right)_s \tag{C.15}$$

or

$$-\frac{w_1^2}{v_1^2} < -\frac{a_1^2}{v_1^2} \tag{C.16}$$

which proves that the flow is superonic upstream of the wave

$$w_1 > a_1 \tag{C.17}$$

For detonation waves, we can apply (C.14) at the downstream state 2 to determine the nature of the flow there. Assuming that the denominator of the r.h.s. is positive, we obtain **Jouguet's rule**: *The flow downstream is subsonic or supersonic if the slope of the Hugoniot is smaller or larger than the slope of the Rayleigh line.* Referring to Fig. 6.5, there are four cases to consider, given in Table C.1. The physically reasonable solutions for both detonations and deflagrations have subsonic states (strong solution) downstream of the wave.

Table C.1: Jouguet's rule for detonations and deflagrations

Case	$a^2 - w^2$	$\partial s/\partial v)_\mathcal{H}$	Note
detonation, U_1	< 0	< 0	strong detonation
detonation, U_2	> 0	> 0	weak detonation
detonation, L_2	< 0	< 0	strong deflagration
detonation, L_1	> 0	> 0	weak deflagration

We can show that the denominator of (C.14) is positive for a shock wave in a perfect gas. The Grüneisen parameter for a perfect gas is a constant and is equal to

$$\mathcal{G} = \gamma - 1 . \tag{C.18}$$

From the perfect gas shock jump conditions (Section A.1), the jump in volume normalized by state 2 is

$$\frac{\Delta v}{v_2} = \frac{-2 + \dfrac{2}{M_1^2}}{\gamma + 1 + \dfrac{2}{M_1^2}} \tag{C.19}$$

so that

$$1 + \mathcal{G}\frac{\Delta v}{2v_2} = \frac{2 + \dfrac{\gamma + 1}{M_1^2}}{\gamma + 1 + \dfrac{2}{M_1^2}} \tag{C.20}$$

$$> 0 \tag{C.21}$$

For large shock speeds, $M_1 \to \infty$, a limiting value is reached

$$\to \frac{2}{\gamma + 1} \tag{C.22}$$

For reacting gases with realistic thermodynamic properties, the Grüneisen parameter has to be computed numerically. The simplest way to do this is to use finite differences to approximate

$$\mathcal{G} = -\frac{v}{T}\left(\frac{\partial T}{\partial v}\right)_s \tag{C.23}$$

The evaluation can be carried out either at frozen composition (gruneisen_fr.m) or equilibrium composition (gruneisen_eq.m). An example of an evaluation of $\mathcal{G}$ and the denominator of (C.6) is shown in Fig. C.1 for states on the Hugoniot near the CJ point of hydrogen-air detonation (see demo_RH_CJ_isentropes.m). The values of both $\mathcal{G}$ and the denominator are approximated by the perfect gas expressions for strong shock waves

$$\mathcal{G} \approx \gamma_s - 1 \tag{C.24}$$

$$\frac{2}{\gamma_s + 1} < 1 + \frac{\mathcal{G}}{2v}\Delta v < 1 \tag{C.25}$$

and the equilibrium value of the isentropic exponent γ_s

$$\gamma_s = -\frac{v}{P}\left(\frac{\partial P}{\partial v}\right)_{s,eq} \tag{C.26}$$
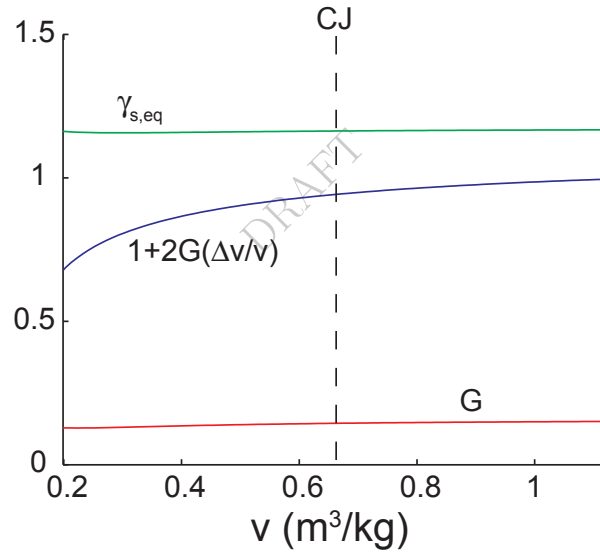

Figure C.1: Grüneisen parameter, denominator of (C.6), and isentropic exponent (C.26) for the example shown in Fig. 6.7.

C.2   Entropy Extremum

The nature of the entropy extremum at the CJ points can be determined by computing the second derivative of entropy along the Hugoniot. This argument is apparently due to Becker (1922) and an alternate presentation is given by Kistiakowsky and Wilson (1941). Proceed by differentiating (C.1) and evaluating at the CJ point, where

$$\left(\frac{\partial s}{\partial v}\right)_{\mathcal{H}} = 0 \quad \text{at the CJ point} \tag{C.27}$$

to obtain

$$\left(\frac{\partial^2 s}{\partial v^2}\right)_{\mathcal{H}} = -\frac{\Delta v}{2T}\left(\frac{\partial^2 p}{\partial v^2}\right)_{\mathcal{H}} \quad \text{at the CJ point} \tag{C.28}$$

Now consider using the differentiation rule embodied by (C.8)

$$\left(\frac{\partial}{\partial v}\right)_{\mathcal{H}} = \left(\frac{\partial}{\partial v}\right)_s + \left(\frac{\partial s}{\partial v}\right)_{\mathcal{H}}\left(\frac{\partial}{\partial s}\right)_v \tag{C.29}$$

twice to compute the derivative

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{\mathcal{H}} = \left(\frac{\partial}{\partial v}\right)_{\mathcal{H}}\left(\frac{\partial P}{\partial v}\right)_{\mathcal{H}} \tag{C.30}$$

$$= \left[\left(\frac{\partial}{\partial v}\right)_s + \left(\frac{\partial s}{\partial v}\right)_{\mathcal{H}}\left(\frac{\partial}{\partial s}\right)_v\right]\left(\frac{\partial P}{\partial v}\right)_s + \left(\frac{\partial}{\partial v}\right)_{\mathcal{H}}\left[\left(\frac{\partial P}{\partial s}\right)_v\left(\frac{\partial s}{\partial v}\right)_{\mathcal{H}}\right] \tag{C.31}$$

Carrying out the differentiation and evaluating at the CJ point, the only remaining non-zero terms are

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{\mathcal{H}} = \left(\frac{\partial^2 P}{\partial v^2}\right)_s + \left(\frac{\partial P}{\partial s}\right)_v\left(\frac{\partial^2 s}{\partial v^2}\right)_{\mathcal{H}} \quad \text{at the CJ point} \tag{C.32}$$

Combining this with the result of (C.28), we have that

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{\mathcal{H}} = \frac{1}{1 + \dfrac{\mathcal{G}}{2v}\Delta v}\left(\frac{\partial^2 P}{\partial v^2}\right)_s \quad \text{at the CJ point} \tag{C.33}$$

the curvatures of the isentrope and Hugoniot have the same sign as long as the denominator is positive. Define the *Fundamental Derivative of Gasdynamics* Thompson (1971) as

$$\Gamma = \frac{v^3}{2a^2}\left(\frac{\partial^2 P}{\partial v^2}\right)_s \tag{C.34}$$

we can write (C.28) to clearly show the sign and verify the dimensional correctness

$$\left(\frac{\partial^2 s}{\partial v^2}\right)_{\mathcal{H}} = \left(\frac{-\Delta v}{v}\right)\cdot\left(\frac{a^2}{Tv^2}\right)\cdot\left(\frac{1}{1 + \mathcal{G}\dfrac{\Delta v}{2v}}\right)\cdot\Gamma \quad \text{at the CJ point.} \tag{C.35}$$

For normal fluids Menikoff and Plohr (1989), the curvature of the isentropes will be positive, $\Gamma > 0$, so that the entropy is a relative minimum at the upper CJ point

$$\left(\frac{\partial^2 s}{\partial v^2}\right)_{\mathcal{H}} > 0 \quad \text{at the upper CJ point} \quad \Delta v < 0 \tag{C.36}$$

and a relative maximum at the lower CJ point

$$\left(\frac{\partial^2 s}{\partial v^2}\right)_{\mathcal{H}} < 0 \quad \text{at the lower CJ point} \quad \Delta v > 0 \tag{C.37}$$

The entropy extremum property has been the source of a great deal of confused speculation and led to the misconception that detonation-based combustors are the most efficient for propulsion. There is a very substantial irreversible entropy rise associated with detonation compared to the modest irreversibility for deflagration. The variation of entropy on the Hugoniot and the implications for propulsion systems are discussed in detail by Wintenberger and Shepherd (2006). From their Abstract, we quote the results:

"For a given stagnation enthalpy, we find that stationary detonation waves generate a higher entropy rise than deflagration waves. The combustion process generating the lowest entropy increment is found to be constant-pressure combustion. These results clearly demonstrate that the minimum entropy property of detonations derived from the conventional Hugoniot analysis does not imply superior performance in all propulsion systems. This finding reconciles previous analysis of flow path performance analysis of detonation-based ramjets with the thermodynamic cycle analysis of detonation-based propulsion systems. We conclude that the thermodynamic analysis of propulsion systems based on stationary detonation waves must be formulated differently than for propagating waves, and the two situations lead to very different results."

C.3   Temperature and Entropy on the Hugoniot

Differentiating the internal energy form of the Hugoniot equation we obtain the relation between changes in internal energy, pressure and specific volume on the Hugoniot

$$de = \frac{1}{2}(v_1 - v)\,dP - \frac{1}{2}(P + P_1)\,dv \ . \tag{C.38}$$

A alternate expression for de is obtained by considering $e(v, T)$ and using thermodynamic identities

$$de = \left(\frac{\mathcal{G}}{v}c_v T - P\right) + c_v dT \ . \tag{C.39}$$

Equating these two expressions, a differential equation for temperature on the Hugoniot is obtained

$$\frac{dT}{dv} = -\frac{\mathcal{G}}{v}T + \frac{1}{2c_v}\left[(v_1 - v)\left(\frac{dP}{dv}\right)_{\mathcal{H}} + P - P_1\right] \ . \tag{C.40}$$

A differential equation for entropy can be obtained by rewriting the fundamental relation of thermodynamics as

$$T\,ds = de + P\,dv\,, \tag{C.41}$$

and evaluating this on the Hugoniot to obtain

$$\frac{ds}{dv} = \frac{1}{T}\left[\left(\frac{de}{dv}\right)_{\mathcal{H}} + P\right] \ . \tag{C.42}$$

From the energy form of the Hugoniot we obtain

$$\left(\frac{de}{dv}\right)_{\mathcal{H}} = \frac{1}{2}\left[(v_1 - v)\left(\frac{dP}{dv}\right)_{\mathcal{H}} - (P + P_1)\right] \ , \tag{C.43}$$

substituting and simplifying we obtain

$$\frac{ds}{dv} = \frac{1}{2T}\left[(v_1 - v)\left(\frac{dP}{dv}\right)_{\mathcal{H}} + P - P_1\right] \ . \tag{C.44}$$

These equations for temperature and entropy can be integrated as a function of volume on the Hugoniot given a relationship $P_{\mathcal{H}}(v)$ and the derivative $\left(\dfrac{dP}{dv}\right)_{\mathcal{H}}$ as well as estimates for the Grüneisen coefficient $\mathcal{G}(v, T)$ and specific heat capacity $c_v(T, v)$. This is a useful strategy that is used when limited thermodynamic data is available about states on the Hugoniot as is often the case in shock compression of liquids and solids.

Appendix D

Real Gas Adiabatic Change Equation

This derivation of the real gas thermicity function is the work of Abbott (1991). Similar to Section 9.2, the derivation begins with expanding pressure as a function of entropy, volume and species amounts. Unlike Section 9.2, the following derivation is carried out with extensive quantities and mole numbers. At the conclusion, the results will be transformed into specific mass properties and compared with the ideal gas results obtained in Section 9.

$$
dP = \left(\frac{\partial P}{\partial V}\right)_{S,\mathbf{N}} dV + \left(\frac{\partial P}{\partial S}\right)_{V,\mathbf{N}} dS + \sum_k \left(\frac{\partial P}{\partial N_k}\right)_{V,S,N_{i\neq k}} dN_k \ . \tag{D.1}
$$

Factoring out the first partial derivative, we obtain

$$
dP = \left(\frac{\partial P}{\partial V}\right)_{S,\mathbf{N}} \left[dV + \left(\frac{\partial P}{\partial S}\right)_{V,\mathbf{N}} \left(\frac{\partial V}{\partial P}\right)_{S,\mathbf{N}} dS \right] + \sum_k \left(\frac{\partial P}{\partial N_k}\right)_{V,S,N_{i\neq k}} dN_k \ . \tag{D.2}
$$

$$
\tag{D.3}
$$

The first term in (D.1)

$$
\left(\frac{\partial P}{\partial V}\right)_{S,\mathbf{N}} \tag{D.4}
$$

can be expressed in terms of frozen sound speed a_f

$$
a_f^2 = -v^2 \left(\frac{\partial P}{\partial v}\right)_{s,\mathbf{Y}} \ , \tag{D.5}
$$

$$
\left(\frac{\partial P}{\partial V}\right)_{S,\mathbf{N}} = -\frac{\rho a_f^2}{V} \ , \tag{D.6}
$$

$$
\tag{D.7}
$$

where $\rho = V/M$, M = total mass of the system.

The second term, the coefficient of dS can be rewritten with the usual rules of manipulation of partial derivatives,

$$
\left(\frac{\partial P}{\partial S}\right)_{V,\mathbf{N}} \left(\frac{\partial V}{\partial P}\right)_{S,\mathbf{N}} = -\left(\frac{\partial V}{\partial S}\right)_{P,\mathbf{N}} \ . \tag{D.8}
$$

We can use the standard results of nonreactive thermodynamics to express this as

$$
\left(\frac{\partial V}{\partial S}\right)_{P,\mathbf{N}} = \frac{\beta V T}{C_p} \ , \tag{D.9}
$$

in terms of the coefficient of thermal expansion

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,\mathbf{N}} , \tag{D.10}$$

and heat capacity

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_{P,\mathbf{N}} . \tag{D.11}$$

The third term in (D.1) requires special consideration. Abbott did so by considering a more general situation described in the Theorem at the end of this section. Using this theorem, we obtain

$$\left(\frac{\partial P}{\partial N_k}\right)_{V,S,N_{i\neq k}} = \rho a_f^2 \left[\frac{\overline{V}_k}{\overline{V}} - \frac{\beta T}{C_p}\overline{S}_k\right] , \tag{D.12}$$

From the definition of the thermodynamic potentials

$$\overline{S}_k = \frac{\overline{H}_k - \overline{G}_k}{T} . \tag{D.13}$$

Switching to the chemical potential notation, $\overline{G}_k = \mu_k$, we obtain the following version of (D.1)

$$\mathrm{d}P = \rho a_f^2 \left[-\frac{\mathrm{d}V}{V} + \frac{\beta T}{C_p}\mathrm{d}S + \sum_k\left(\frac{\overline{V}_k}{\overline{V}} - \frac{\beta}{C_p}\overline{H}_k\right)\mathrm{d}N_k + \frac{\beta}{C_p}\sum_k \mu_k \mathrm{d}N_k\right] \tag{D.14}$$

D.1   Thermicity

As discussed in Chapter 9, the fundamental relationship of thermodynamics

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P + \sum_k \mu_k \mathrm{d}N_k , \tag{D.15}$$

and the energy equation for adiabatic flow

$$\mathrm{d}H = V\mathrm{d}P , \tag{D.16}$$

implies that the entropy change is

$$\mathrm{d}S = -\frac{1}{T}\sum_k \mu_k \mathrm{d}N_k . \tag{D.17}$$

Substituting this into (D.14), we find that the entropy change is exactly balanced by the change in Gibbs energy resulting in the cancelation of the second and fourth terms in the adiabatic change equation. Transforming to mass fraction variables

$$\mathrm{d}N_k = \frac{M}{\mathcal{W}_k}\mathrm{d}Y_k , \tag{D.18}$$

defining the specific heat per unit mass

$$c_p = \frac{C_p}{M} , \tag{D.19}$$

and molar volume

$$\overline{V} = \frac{V}{N} \ , \tag{D.20}$$

we obtain the following real-gas version of the adiabatic change equation:

$$\boxed{\frac{\mathrm{d}P}{\mathrm{d}t} = a_f^2 \frac{\mathrm{d}\rho}{\mathrm{d}t} + \rho a_f^2 \underbrace{\sum_k \left(\frac{\mathcal{W}}{\mathcal{W}_k} \frac{\overline{V}_k}{\overline{V}} - \frac{\beta}{c_p} \frac{\overline{H}_k}{\mathcal{W}_k} \right) \frac{\mathrm{d}Y_k}{\mathrm{d}t}}_{\dot{\sigma}}} \tag{D.21}$$

Defining $\dot{\sigma}$ as the thermicity as in Chapter 9, we have

$$\boxed{\dot{\sigma} = \sum_k \left(\frac{\mathcal{W}}{\mathcal{W}_k} \frac{\overline{V}_k}{\overline{V}} - \frac{\beta}{c_p} \frac{\overline{H}_k}{\mathcal{W}_k} \right) \frac{\mathrm{d}Y_k}{\mathrm{d}t} \ .} \tag{D.22}$$

and the adiabatic change equation can be written compactly as

$$\frac{\mathrm{d}P}{\mathrm{d}t} = a_f^2 \frac{\mathrm{d}\rho}{\mathrm{d}t} + \rho a_f^2 \dot{\sigma} \tag{D.23}$$

which is identical to the previous development and provided an alternative formulation of thermicity enabling the computation using partial molar properties instead of mass fractions. This is more convenient for working with the many dense gas equations of state that have developed by the chemical engineering community.

D.2 Abbott's Theorem: Derivative of Intensive Properties by Extensive Properties

Assume that an intensive property W depends on extensive properties A, B and species mole numbers $\{N_k\}$. Let X and Y be two intensive quantities (one of which may be W). Define the two generalized partial molar properties $\widehat{A}$ and $\widehat{B}$

$$\widehat{A}_k = \left(\frac{\partial A}{\partial N_k} \right)_{X,Y,N_{i \neq k}} \ , \tag{D.24}$$

$$\widehat{B}_k = \left(\frac{\partial B}{\partial N_k} \right)_{X,Y,N_{i \neq k}} \ . \tag{D.25}$$

Then for $W(A, B, \mathbf{N})$ we have:

$$\boxed{\left(\frac{\partial W}{\partial N_k} \right)_{A,B,N_{i \neq k}} = \left(\frac{\partial W}{\partial N_k} \right)_{X,Y,N_{i \neq k}} - \left(\frac{\partial W}{\partial A} \right)_{B,\mathbf{N}} \widehat{A}_i - \left(\frac{\partial W}{\partial B} \right)_{A,\mathbf{N}} \widehat{B}_i} \tag{D.26}$$

The proof proceeds by apply the chain rule of differentiation considering A and B as a function of the species mole amounts N_k.

$$\mathrm{d}W = \left(\frac{\partial W}{\partial A} \right)_{B,\mathbf{N}} \mathrm{d}A + \left(\frac{\partial W}{\partial B} \right)_{A,\mathbf{N}} \mathrm{d}B + \sum_k \left(\frac{\partial W}{\partial N_k} \right)_{N_{i \neq k}} \mathrm{d}N_k \tag{D.27}$$

Dividing by $\mathrm{d}N_k$ and restricting differentiation to constant (X, Y), we obtain

$$\left(\frac{\partial W}{\partial N_k} \right)_{X,Y,N_{i \neq k}} = \left(\frac{\partial W}{\partial A} \right)_{B,\mathbf{N}} \left(\frac{\partial A}{\partial N_k} \right)_{X,Y,N_{i \neq k}} + \left(\frac{\partial W}{\partial B} \right)_{A,\mathbf{N}} \left(\frac{\partial B}{\partial N_k} \right)_{X,Y,N_{i \neq k}} + \left(\frac{\partial W}{\partial N_k} \right)_{A,B,N_{i \neq k}} \tag{D.28}$$

Rearranging and simplifying using the previous definitions of $\widehat{A}_i$ and $\widehat{B}_i$, we obtain the desired result.

D.3 Application

Using the theorem just demonstrated, make the following assignments:

$$A = V \ , \tag{D.29}$$

$$B = S \ , \tag{D.30}$$

$$W = Y = P \ , \tag{D.31}$$

$$X = T \ . \tag{D.32}$$

For these choices

$$\left(\frac{\partial W}{\partial N_k} \right)_{X,Y,N_{i \neq k}} = \left(\frac{\partial P}{\partial N_k} \right)_{T,P,N_{i \neq k}} \equiv 0 \ . \tag{D.33}$$

The generalized partial molar properties can be expressed in term of the conventional partial molar properties

$$\widehat{A} = \left(\frac{\partial V}{\partial N_k} \right)_{T,P,N_{i \neq k}} = \overline{V}_k \ , \tag{D.34}$$

$$\widehat{B} = \left(\frac{\partial S}{\partial N_k} \right)_{T,P,N_{i \neq k}} = \overline{S}_k \ , \tag{D.35}$$

and the theorem yields

$$\left(\frac{\partial P}{\partial N_k} \right)_{V,S,N_{i \neq k}} = - \left(\frac{\partial P}{\partial V} \right)_{S,\mathbf{N}} \overline{V}_k - \left(\frac{\partial P}{\partial S} \right)_{V,\mathbf{N}} \overline{S}_k \ . \tag{D.36}$$

The partial derivatives can be expressed in terms of standard property definitions using thermodynamic identities.

$$\left(\frac{\partial P}{\partial V} \right)_{S,\mathbf{N}} = - \frac{\rho a_f^2}{V} \ , \tag{D.37}$$

$$\left(\frac{\partial P}{\partial S} \right)_{V,\mathbf{N}} = \rho a_f^2 \frac{\beta T}{C_p} \ . \tag{D.38}$$

The final result is

$$\boxed{\left(\frac{\partial P}{\partial N_k} \right)_{V,S,N_{i \neq k}} = \rho a_f^2 \left[\frac{\overline{V}_k}{V} - \frac{\beta T}{C_p} \overline{S}_k \right]} \tag{D.39}$$

Appendix E

Classical Thermodynamics

This appendix provides a brief summary of classical thermodynamic relations for a single-phase, constant-composition substance. Relationships are presented using mass-specific quantities.

> "Thermodynamics is an experimental science, and not a branch of metaphysics. It consists of a collection of equations, and also some inequalities, which inter-relate certain kinds of measurable physical quantities. In any thermodynamic equation every quantity is independently measurable. What can such an equation 'tell one' about one's system or process? Or, in other words, what can we learn from such an equation about the microscopic explanation of macroscopic change? Nothing whatsoever. What then is the use of thermodynamic equations? They are useful because some quantities are easier to measure than others." - McGlashan (1979)

E.1 Thermodynamic potentials and fundamental relations

$$
\begin{aligned}
\textbf{energy} \quad & e(s,v) \\
\mathrm{d}e &= T\,\mathrm{d}s - P\,\mathrm{d}v & \text{(E.1)} \\
\textbf{enthalpy} \quad h(s,P) &= e + Pv \\
\mathrm{d}h &= T\,\mathrm{d}s + v\,\mathrm{d}P & \text{(E.2)} \\
\textbf{Helmholtz} \quad a(T,v) &= e - Ts \\
\mathrm{d}a &= -s\,\mathrm{d}T - P\,\mathrm{d}v & \text{(E.3)} \\
\textbf{Gibbs} \quad g(T,P) &= e - Ts + Pv \\
\mathrm{d}g &= -s\,\mathrm{d}T + v\,\mathrm{d}P & \text{(E.4)}
\end{aligned}
$$

E.2 Maxwell relations

$$
\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v \tag{E.5}
$$

$$
\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P \tag{E.6}
$$

$$
\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v \tag{E.7}
$$

$$
\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P \tag{E.8}
$$

Calculus identities:

$$F(x,y,\dots) \qquad \mathrm{d}F = \left(\frac{\partial F}{\partial x}\right)_{y,z,\dots} \mathrm{d}x + \left(\frac{\partial F}{\partial y}\right)_{x,z,\dots} \mathrm{d}y + \dots \tag{E.9}$$

$$\left(\frac{\partial x}{\partial y}\right)_f = -\frac{\left(\frac{\partial f}{\partial y}\right)_x}{\left(\frac{\partial f}{\partial x}\right)_y} \tag{E.10}$$

$$\left(\frac{\partial x}{\partial f}\right)_y = \frac{1}{\left(\frac{\partial f}{\partial x}\right)_y} \tag{E.11}$$

E.3 Various defined quantities

specific heat at constant volume $\quad c_v \;\equiv\; \left(\dfrac{\partial e}{\partial T}\right)_v \hfill \text{(E.12)}$

specific heat at constant pressure $\quad c_p \;\equiv\; \left(\dfrac{\partial h}{\partial T}\right)_P \hfill \text{(E.13)}$

ratio of specific heats $\quad \gamma \;\equiv\; \dfrac{c_p}{c_v} \hfill \text{(E.14)}$

sound speed $\quad a \;\equiv\; \sqrt{\left(\dfrac{\partial P}{\partial \rho}\right)_s} \hfill \text{(E.15)}$

coefficient of thermal expansion $\quad \beta \;\equiv\; \dfrac{1}{v}\left(\dfrac{\partial v}{\partial T}\right)_P \hfill \text{(E.16)}$

isothermal compressibility $\quad K_T \;\equiv\; -\dfrac{1}{v}\left(\dfrac{\partial v}{\partial P}\right)_T \hfill \text{(E.17)}$

isentropic compressibility $\quad K_s \;\equiv\; -\dfrac{1}{v}\left(\dfrac{\partial v}{\partial P}\right)_s = \dfrac{1}{\rho a^2} \hfill \text{(E.18)}$

thermal pressure coefficient $\quad \left(\dfrac{\partial P}{\partial T}\right)_v \;\equiv\; c_v \dfrac{\mathcal{G}}{v} \hfill \text{(E.19)}$

$$\equiv \frac{\beta}{K_T} \tag{E.20}$$

$$\equiv \rho a^2 \beta \frac{c_v}{c_p} \tag{E.21}$$

Joule-Thompson coefficient $\quad \equiv\; \left(\dfrac{\partial P}{\partial T}\right)_h = \dfrac{v}{c_p}\left(\beta T - 1\right) \hfill \text{(E.22)}$

Specific heat relationships

$$\gamma \equiv \frac{c_p}{c_v} = \frac{K_T}{K_s} \quad \text{or} \quad \left(\frac{\partial P}{\partial v}\right)_s = \gamma \left(\frac{\partial P}{\partial v}\right)_T \tag{E.23}$$

$$c_p - c_v = -T \left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P^2 \tag{E.24}$$

$$= T\frac{v\beta^2}{K_T} \tag{E.25}$$

$$= T a^2 \beta^2 \frac{c_v}{c_p} \tag{E.26}$$

Fundamental derivative

$$
\Gamma \equiv \frac{a^4}{2v^3} \left.\frac{\partial^2 v}{\partial P^2}\right)_s \tag{E.27}
$$

$$
= \frac{v^3}{2a^2} \left(\frac{\partial^2 P}{\partial v^2}\right)_s \tag{E.28}
$$

$$
= 1 + \rho a \left(\frac{\partial a}{\partial P}\right)_s \tag{E.29}
$$

$$
= \frac{1}{2}\left(\frac{v^2}{a^2}\left(\frac{\partial^2 h}{\partial v^2}\right)_s + 1\right) \tag{E.30}
$$

$$
= -\frac{v}{2}\frac{\left(\frac{\partial^2 P}{\partial v^2}\right)_s}{\left(\frac{\partial P}{\partial v}\right)_s} \tag{E.31}
$$

$$
\left(\frac{\partial^2 P}{\partial v^2}\right)_s = \left(\frac{\partial^2 P}{\partial v^2}\right)_T - \frac{3T}{c_v}\left(\frac{\partial P}{\partial v}\right)_T\left(\frac{\partial^2 P}{\partial v \partial T}\right) + \frac{3T}{c_v^2}\left(\frac{\partial P}{\partial T}\right)_v^2\left(\frac{\partial c_v}{\partial v}\right)_T \tag{E.32}
$$

$$
+ \frac{T}{c_v^3}\left(\frac{\partial P}{\partial T}\right)_v^3\left[1 - \frac{T}{c_v}\left(\frac{\partial c_v}{\partial T}\right)_v\right] \text{ Bethe 1942} \tag{E.33}
$$

Sound speed (squared)

$$
a^2 \equiv \left(\frac{\partial P}{\partial \rho}\right)_s \tag{E.34}
$$

$$
= -v^2\left(\frac{\partial P}{\partial v}\right)_s \tag{E.35}
$$

$$
= \frac{v}{K_s} \tag{E.36}
$$

$$
= \gamma\frac{v}{K_T} \tag{E.37}
$$

$$
= v^2\frac{\left(\frac{\partial e}{\partial v}\right)_P + P}{\left(\frac{\partial e}{\partial P}\right)_v} \tag{E.38}
$$

$$
= \frac{\left(\frac{\partial h}{\partial \rho}\right)_P}{\frac{1}{\rho} - \left(\frac{\partial h}{\partial P}\right)_\rho} \tag{E.39}
$$

Grüneisen Coefficient

$$
\mathcal{G} \;\equiv\; \frac{v\beta}{c_v K_T} \tag{E.40}
$$

$$
= \; v\left(\frac{\partial P}{\partial e}\right)_v \tag{E.41}
$$

$$
= \; \frac{v\beta}{c_p K_s} \tag{E.42}
$$

$$
= \; \frac{a^2\beta}{c_p} \tag{E.43}
$$

$$
= \; -\frac{v}{T}\left(\frac{\partial T}{\partial v}\right)_s \tag{E.44}
$$

$$
= \; \frac{v}{T}\left(\frac{\partial P}{\partial s}\right)_v \tag{E.45}
$$

$$
= \; \frac{v}{c_v}\left(\frac{\partial P}{\partial T}\right)_v \tag{E.46}
$$

E.4 $v(P,s)$ relation

$$
\frac{\mathrm{d}v}{v} \;=\; -K_s\,\mathrm{d}P + \Gamma(K_s\,\mathrm{d}P)^2 + \beta\frac{T\,\mathrm{d}s}{c_p} + \dots \tag{E.47}
$$

$$
= \; -\frac{\mathrm{d}P}{\rho a^2} + \Gamma\left(\frac{\mathrm{d}P}{\rho a^2}\right)^2 + \mathcal{G}\frac{T\mathrm{d}s}{a^2} + \dots \tag{E.48}
$$

E.5   Equation of State Construction

Given $c_v(v,T)$ and $P(v,T)$, integrate

$$
\mathrm{d}e \;=\; c_v\,\mathrm{d}T + \left(T\left(\frac{\partial P}{\partial T}\right)_v - P\right)\mathrm{d}v \tag{E.49}
$$

$$
\mathrm{d}s \;=\; \frac{c_v}{T}\,\mathrm{d}T + \left(\frac{\partial P}{\partial T}\right)_v \mathrm{d}v \tag{E.50}
$$

along two paths: I: variable T, fixed ρ and II: variable ρ, fixed T.

Energy:

$$
e = e_\circ + \underbrace{\int_{T_\circ}^{T} c_v(T,\rho_\circ)\,\mathrm{d}T}_{\text{I}} + \underbrace{\int_{\rho_\circ}^{\rho}\left(P - T\left(\frac{\partial P}{\partial T}\right)_\rho\right)\frac{\mathrm{d}\rho}{\rho^2}}_{\text{II}} \tag{E.51}
$$

Ideal gas limit $\rho_\circ \to 0$,

$$
\lim_{\rho_\circ \to 0} c_v(T,\rho_\circ) = c_v^{ig}(T) \tag{E.52}
$$

The ideal gas limit of I is the ideal gas internal energy

$$
e^{ig}(T) = \int_{T_\circ}^{T} c_v^{ig}(T)\,\mathrm{d}T \tag{E.53}
$$

Ideal gas limit of II is the *departure function*

$$
e^{d}(\rho,T) = \int_{0}^{\rho}\left(P - T\left(\frac{\partial P}{\partial T}\right)_\rho\right)\frac{\mathrm{d}\rho}{\rho^2} \tag{E.54}
$$

and the complete expression for internal energy is

$$e(\rho, T) = e_\circ + e^{ig}(T) + e^d(\rho, T) \tag{E.55}$$

Entropy:

$$s = s_\circ + \underbrace{\int_{T_\circ}^T \frac{c_v(T, \rho_\circ)}{T} \, \mathrm{d}T}_{\text{I}} + \underbrace{\int_{\rho_\circ}^\rho \left(-\left(\frac{\partial P}{\partial T} \right)_\rho \right) \frac{\mathrm{d}\rho}{\rho^2}}_{\text{II}} \tag{E.56}$$

The ideal gas limit $\rho_\circ \to 0$ has to be carried out slightly differently since the ideal gas entropy, unlike the internal energy, is a function of density and is singular at $\rho = 0$. Define

$$s^{ig} = \int_{T_\circ}^T \frac{c_v^{ig}(T)}{T} \, \mathrm{d}T - R \int_{\rho_\circ}^\rho \frac{\mathrm{d}\rho}{\rho} \tag{E.57}$$

where the second integral on the RHS is $R \ln \rho_\circ / \rho$. Then compute the departure function by subtracting the singular part before carrying out the integration

$$s^d(\rho, T) = \int_0^\rho \left(R - \frac{1}{\rho} \left(\frac{\partial P}{\partial T} \right)_\rho \right) \frac{\mathrm{d}\rho}{\rho} \tag{E.58}$$

and the complete expression for entropy is

$$s(\rho, T) = s_\circ + s^{ig}(\rho, T) + s^d(\rho, T) \tag{E.59}$$

DRAFT

Appendix F

Physical Constants of Selected Molecules

The critical constants of selected molecules and Lennard-Jones (LJ) potential parameters for selected fluids are given in the following table. The LJ parameters are taken from the transport databases used for Cantera (Goodwin et al., 2017).

Table F.1: Critical Constants (Rumble, 2018) and LJ parameters (Cloutman, 2000, Kee et al., 1998) for selected molecular fluids .

Species	$\mathcal{W}$ (g/mol)	P_c (MPa)	T_c (K)	ρ_c (kg/m^3)	Z_c	ϵ/k_B (K)	ϱ (nm)
H$_2$	2.016	1.30	33.2	31.04	0.305	38.0	0.292
CO$_2$	44.01	7.38	304.	466.	0.275	244.0	0.3763
N$_2$	28.02	3.40	126.	314.	0.290	97.53	0.3621
O$_2$	32.00	5.04	155.	435.	0.289	107.4	0.3458
H$_2$O	18.01	22.1	647.	323.	0.230	572.4	0.2605
NO	30.01	6.48	180.	516.	0.252	97.53	0.3621
CO	28.01	3.50	134.	311.	0.274	98.1	0.365
Ar	39.95	4.90	151.	536.	0.291	136.5	0.33
He	4.00	0.227	5.20	69.	0.308	10.2	0.2576

F.1 Diatomic Molecule Energy Levels

The molecular electronic, vibrational and rotational states for many diatomic molecules are tabulated in two NIST data bases: diatomic spectra and chemistry webbook See p. 73-83 and Eq. 2.97 of Boyd and Schwartzentruber (2017) to translate the spectroscopic symbols for molecular states into degeneracy factors. States for all of these atoms and molecules (including NO and NO+) are tabulated in Park (1990), at the end of Chapter 1. Chapter 9 and 10 of Hanson et al. (2016) and Bernath (2016) give a more in depth discussion of the fundamentals of electronic structure of atoms and molecules.

The energy levels derived from spectroscopic measurement for diatomic molecules are given in term of expansions in integer powers of the rotational and vibrational level quantum numbers (v, J). One way of doing this is to use the *Dunham* coefficients $Y_{k,l}$ and the formula

$$E(v, J) = \sum_{k,l} Y_{k,l} (v + 1/2)^k [J(J+1)]^l \ . \tag{F.1}$$

Many papers and some databases, particularly the multivolume compilations of Herzberg and Huber *Molecular Spectra and Molecular Structure*, use a different nomenclature and a translational table between conventional and Dunham notation is given below.

$k \setminus l$	0	1	2	3	4
0		B_e	$-D_e$	H_e	L_e
1	ω_e	$-\alpha_e$	$-\beta_e$		
2	$-\omega_e x_e$	γ_e			
3	$\omega_e y_e$				
4	$\omega_e z_e$				

Constants using the historical notation are given for selected diatomic molecules and some relevant excited states are given in Table F.2. The energy levels are computed as follows accounting for the conversion from wavenumber units (cm^{-1}) to Joule.

$$E = E_{rot} + E_{vib} + E_{ele} \tag{F.2}$$

$$E_{rot}/hc = B_v(J+1) - D_v J(J+1)^2 \tag{F.3}$$

where

$$B_v = B_e - \alpha_e(v+1/2) \tag{F.4}$$

$$E_{vib}/hc = \omega_e(v+1/2) - \omega_e x_e(v+1/2)^2 \tag{F.5}$$

$$E_{ele}/hc = T_e \tag{F.6}$$

Table F.2: Diatomic molecular constants for selected species. Spectroscopic constants from NIST Chemistry WebBook

	State	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	D_v (cm^{-1})	r_e (nm)
Ground States
N$_2$	X$^1\Sigma_g^+$	2358.560	14.320	1.9982360	0.0173100	5.737×10^{-6}	0.1097690
NO	X$^2\Pi_{1/2}$	1904.200	14.070	1.6719500	0.0171000	0.5×10^{-6}	0.1150770
O$_2$	X$^3\Sigma_g^-$	1580.190	11.980	1.4456220	0.0159330	4.839×10^{-6}	0.1207520
H$_2$	X$^1\Sigma_g$	4401.210	121.340	60.8530000	3.0620000	0.0471	0.0741440
CO	X$^1\Sigma^+$	2169.810	13.290	1.9312810	0.0175044	6.1216×10^{-6}	0.1128320
OH	X$^1\Pi_i$	3737.760	84.881	18.910	0.724	0.001938	0.0970
Excited Electronic States
NO*	A$^2\Sigma^+$	2374.31	10.106	1.9965	0.01915	5.47×10^{-6}	0.106434
OH*	A$^2\Sigma^+$	3178.8	92.91	17.358	0.786	0.002039	0.10121
O$_2^*$	B$^3\Sigma_u^-$	709.31	10.65	0.819	0.01206	4.55×10^{-6}	0.16042

Electronic excitation energy T_e

NO*	43965.7	(cm^{-1})
OH*	32684.1	(cm^{-1})
O$_2^*$	49793.28	(cm^{-1})

Table F.3 gives values of constants for diatomic molecules useful for approximate computations with rigid rotator, harmonic oscillator models of specific heats and dissociation energies that can be used with the ideal dissociating gas model.

Table F.3: Diatomic molecule symmetry factor, rotation and vibration quanta and dissociation energy expressed as temperatures $\Theta = \Delta E / k_b$.

Species	σ	Θ_r (K)	Θ_v (K)	Θ_d (K)
H_2	2	87.5	6,325	52,000
N_2	2	2.89	3,393	113,400
O_2	2	2.08	2,273	59,000
CO	1	2.78	3,122	129,000
NO	1	2.45	2,719	75,490
OH	1	27.9	5,377	52,197
CH	1	20.8	4,113	40,200