Review of Thermodynamics

The equations of stellar structure involve derivatives of thermodynamic variables such as pressure, temperature, and density. To express these derivatives in a useful form, we will need to review the basic thermodynamic relations. First, let's define the variables:

ρ: the gas density
P: the gas pressure
T: the gas temperature
μ: the mean molecular weight
q: the specific heat content
u: the specific internal energy
s: the specific entropy
V: the specific volume ($1/\rho$)

Note that q, u, s, and V are all **per unit mass**. From these variables come the specific heats

$$c_V = \left(\frac{dq}{dT}\right)_V = T\left(\frac{\partial s}{\partial T}\right)_V \tag{1.1}$$

$$c_P = \left(\frac{dq}{dT}\right)_P = T\left(\frac{\partial s}{\partial T}\right)_P \tag{1.2}$$

the ratio of the specific heats

$$\gamma = \frac{c_P}{c_V} \tag{1.3}$$

the adiabatic temperature gradient

$$\nabla_{\rm ad} = \left(\frac{\partial \ln T}{\partial \ln P}\right)_s \tag{1.4}$$

an isothermal compressibility coefficient

$$\alpha = -\frac{P}{V}\left(\frac{\partial V}{\partial P}\right)_{T,\mu} = \left(\frac{\partial \ln \rho}{\partial \ln P}\right)_{T,\mu} \tag{1.5}$$

a volume coefficient of expansion

$$\delta = \frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_{P,\mu} = -\left(\frac{\partial \ln \rho}{\partial \ln T}\right)_{P,\mu} \tag{1.6}$$

and a chemical potential coefficient

$$\varphi = -\frac{\mu}{V}\left(\frac{\partial V}{\partial \mu}\right)_{P,T} = \left(\frac{\partial \ln \rho}{\partial \ln \mu}\right)_{P,T} \tag{1.7}$$

(For the following, we will assume the chemical composition is fixed.)

We will also need the first law of thermodynamics:

$$dq = T ds = du + P\, dV \tag{1.8}$$

Note that although there are four variables in this equation (s, T, P, and V), only two are independent.

To derive the relationships between the various thermodynamic variables, first take s and V as independent, and re-write (1.8) as

$$du = T ds - P\,dV \tag{1.9}$$

However, when written in terms of s and V, du is formally

$$du = \left(\frac{\partial u}{\partial s}\right)_V ds + \left(\frac{\partial u}{\partial V}\right)_s dV$$

which means that

$$\left(\frac{\partial u}{\partial s}\right)_V = T \qquad \text{and} \qquad \left(\frac{\partial u}{\partial V}\right)_s = -P \tag{1.10}$$

Now, mathematically

$$\frac{\partial^2 u}{\partial V \partial s} = \frac{\partial^2 u}{\partial s \partial V}$$

so

$$\left(\frac{\partial u}{\partial V}\right)_s \left(\frac{\partial u}{\partial s}\right)_V = \left(\frac{\partial u}{\partial s}\right)_V \left(\frac{\partial u}{\partial V}\right)_s$$

or

$$\left(\frac{\partial T}{\partial V}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_V \tag{1.11}$$

Similarly, if we choose s and P as the independent variables, and add $d(PV)$ to each side of (1.9), then the first law of thermodynamics becomes

$$dH = d(u + PV) = T ds - P dV + P dV + V dP = T ds + V dP$$

The total first derivative of H is then

$$dH = \left(\frac{\partial H}{\partial s}\right)_P ds + \left(\frac{\partial H}{\partial P}\right)_s dP$$

which implies that

$$\left(\frac{\partial H}{\partial s}\right)_P = T \qquad \text{and} \qquad \left(\frac{\partial H}{\partial P}\right)_s = V$$

and

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial V}{\partial s}\right)_P \tag{1.12}$$

If we subtract $d(Ts)$ from each side of the first law of thermodynamics, then T and V are the free parameters, via

$$dF = d(u - Ts) = Tds - PdV - Tds - sdT = -PdV - sdT$$

We then get the relations

$$\left(\frac{\partial F}{\partial T}\right)_V = -s \qquad \text{and} \qquad \left(\frac{\partial F}{\partial V}\right)_T = -P$$

which leads via the second derivatives to

$$\left(\frac{\partial s}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{1.13}$$

Finally, if T and P are chosen to be independent, and $d(PV - Ts)$ are added to (1.8), then we can derive the relation

$$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{1.14}$$

Thus, we have Maxwell's relations

$$\left(\frac{\partial T}{\partial V}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_V \tag{1.11}$$

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial V}{\partial s}\right)_P \tag{1.12}$$

$$\left(\frac{\partial s}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{1.13}$$

$$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{1.14}$$

To derive a relation between the specific heats, start by letting T and P be independent, and write the specific heat content as

$$dq = Tds = T\left[\left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP\right]$$

and dP as

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

This gives

$$dq = T\left(\frac{\partial s}{\partial T}\right)_P dT + T\left(\frac{\partial s}{\partial P}\right)_T \left[\left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV\right]$$

We can now evaluate (dq/dT) while holding V constant, *i.e.*, with $dV = 0$

$$\left(\frac{dq}{dT}\right)_V = T\left(\frac{\partial s}{\partial T}\right)_P + T\left(\frac{\partial s}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V$$

The term on the left side of the equation is c_V, the first term on the right is c_P, and $(ds/dP)_T = -(dV/dT)_P$ by a Maxwell relation (1.14). Thus,

$$c_P - c_V = T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V$$

The first partial differential can immediately be written in terms of the volume coefficient of expansion (1.6)

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V\delta}{T} \tag{1.15}$$

The second partial differential can also be re-written, if one first notes that the total derivative for dV is

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

Thus, when V is held constant, $dV = 0$, and

$$\left(\frac{\partial P}{\partial T}\right)_V = - \left(\frac{\partial V}{\partial T}\right)_P \Big/ \left(\frac{\partial V}{\partial P}\right)_T$$

The numerator on the right side is again $(\delta/\rho T)$, while the denominator is related to the compressibility coefficient by

$$\left(\frac{\partial V}{\partial P}\right)_T = -\frac{\alpha V}{P}$$

Thus

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{P\delta}{T\alpha} \tag{1.16}$$

and

$$c_P - c_V = \frac{PV\delta^2}{T\alpha} = \frac{P\delta^2}{\rho T\alpha} \tag{1.17}$$

Note that this reduces to $\mathcal{R} = k/m_A$ for an ideal gas.

Finally, to express the change in the heat content of a system, dq, in terms of the intensive parameters only, choose V and T as the independent variables, and write the change in entropy as

$$ds = \left(\frac{\partial s}{\partial T}\right)_V dT + \left(\frac{\partial s}{\partial V}\right)_T dV$$

Using the definition of heat capacity (1.1) and the Maxwell relation (1.13), this becomes

$$ds = \frac{c_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

If we now substitude (1.16) for $(\partial P/\partial T)_V$, and convert dV to $d\rho$ using $dV = -1/\rho^2\, d\rho$, we get an expression for dq

$$dq = Tds = c_V dT - \frac{P\delta}{\rho\alpha}\frac{d\rho}{\rho}$$

This can then be further simplified by noting that

$$\frac{d\rho}{\rho} = \left(\frac{\partial \ln \rho}{\partial \ln P}\right)_T d\ln P + \left(\frac{\partial \ln \rho}{\partial \ln T}\right)_P d\ln T = \alpha\frac{dP}{P} - \delta\frac{dT}{T}$$

Thus

$$dq = c_V dT + \frac{P\delta^2}{\rho T\alpha} dT - \frac{\delta}{\rho} dP$$

or

$$dq = c_P dT - \frac{\delta}{\rho} dP \tag{1.18}$$

This equation also leads directly to an expression for the adiabatic temperature gradient. If $dq = 0$, then

$$c_P dT = \frac{\delta}{\rho} dP$$

which implies that

$$\left(\frac{\partial T}{\partial P}\right)_s = \frac{\delta}{\rho c_P}$$

and

$$\nabla_{\rm ad} = \left(\frac{\partial \ln T}{\partial \ln P}\right)_s = \frac{P\delta}{T\rho c_P} \tag{1.19}$$

Note that for an ideal gas, the definition of an adiabat implies that

$$P \propto \rho^\gamma \propto \left(\frac{P}{T}\right)^\gamma \Longrightarrow T \propto P^{(\gamma-1)/\gamma}$$

Hence for a monotonic gas with $\gamma = 5/3$,

$$\nabla_{\rm ad} = (2/3)\Big/(5/3) = 0.4 \tag{1.20}$$

Note also that (1.19) can then be substituted back into (1.18) to yield an equation for dq in terms of P, T, c_P, and adiabatic temperature gradient

$$dq = c_P dT - \frac{T c_P \nabla_{\rm ad}}{P} dP = c_P T \left[\frac{dT}{T} - \nabla_{\rm ad}\frac{dP}{P}\right] \tag{1.21}$$