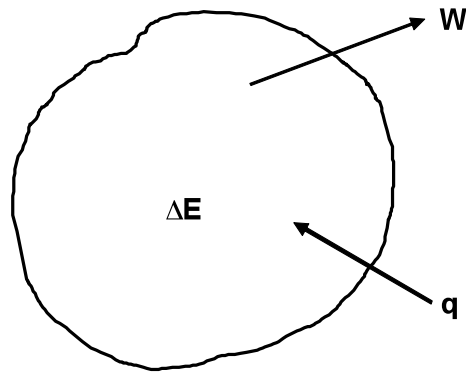


**May 31, 2010**  
**CLASSICAL THERMODYNAMICS**  
**by Paul Paslay, P.E. #44278**

**FIRST LAW**

Define a system as a fixed mass enclosed in a single surface boundary

**THE SYSTEM**



**$\Delta E$  = change in internal energy of system**  
 **$W$  = work done by system**  
 **$q$  = heat flow into system**

The first law of Thermodynamics is a statement of conservation of energy for a system undergoing a thermodynamic change.

$$\Delta E = q - W$$

In classical thermodynamics the development is simplified by assuming the state of the system is dependent on only three variables that are related through an equation of state.

Variables and equation of state:

$$f(P, V, T) = 0$$

where,

$P$  = pressure

$V$  = volume

$T$  = temperature, the exact scale to be used is defined later

Define the specific heat at constant  $V$  for the system as,

$$C_V = \left. \frac{\partial E}{\partial T} \right|_V$$

Define the specific heat at constant P for the system as,

$$C_P = \left. \frac{\partial (E + P \cdot V)}{\partial T} \right|_P$$

The internal energy may be considered as  $E(V, T)$  in view of the equation of state so that,

$$dE = \left. \frac{\partial E}{\partial V} \right|_T \cdot dV + \left. \frac{\partial E}{\partial T} \right|_V \cdot dT$$

Differentiating again with respect to T yields,

$$\left. \frac{\partial E}{\partial T} \right|_P = \left. \frac{\partial E}{\partial V} \right|_T \cdot \left. \frac{\partial V}{\partial T} \right|_P + \left. \frac{\partial E}{\partial T} \right|_V$$

so that,

$$C_P - C_V = \left( P + \left. \frac{\partial E}{\partial V} \right|_T \right) \cdot \left. \frac{\partial V}{\partial T} \right|_P$$

Define the enthalpy, H, as,

$$H \equiv E + P \cdot V$$

The Joule-Thompson coefficient,  $\mu_{J.T.}$ , is defined as,

$$\mu_{J.T.} = \left. \frac{\partial T}{\partial P} \right|_H$$

### **Ideal Gas**

Temporarily consider the thermodynamic system to be a fixed mass of an ideal gas.

First part of definition of an ideal gas.

$$P \cdot V = R \cdot T, \quad R = 1.386 \frac{\text{Btu}}{(\text{lb} - \text{mol}) \cdot ^\circ \text{F}}$$

An early experimental result by Joule is adopted as the other part of the definition of an ideal gas.

Joule's experiment  $\rightarrow \left. \frac{\partial E}{\partial V} \right|_T = 0$

In this case,

$$dE = \left. \frac{\partial E}{\partial V} \right|_T \cdot dV + \left. \frac{\partial E}{\partial T} \right|_V \cdot dT = \left. \frac{\partial E}{\partial T} \right|_V \cdot dT$$

Therefore  $E = E(T)$  and

$$1 \quad C_V = C_V(T), \quad C_P - C_V = P \cdot \left. \frac{\partial V}{\partial T} \right|_P = R, \quad C_P = C_P(T), \quad \gamma = \frac{C_P}{C_V}$$

$$2. \quad \Delta E = \int_{T_1}^{T_2} C_V \cdot dT \quad \Delta H = \int_{T_1}^{T_2} C_P \cdot dT$$

$$3. \quad \text{For reversible isothermal process} \quad q = W = R \cdot T \cdot \ln\left(\frac{V_2}{V_1}\right) = R \cdot T \cdot \ln\left(\frac{P_1}{P_2}\right)$$

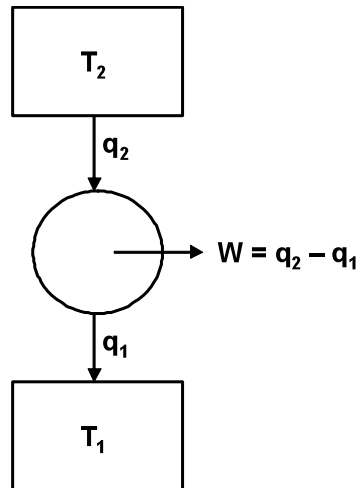
$$4. \quad \text{For reversible adiabatic process} \quad W = - \int_{T_1}^{T_2} C_V \cdot dT \quad C_V \cdot \frac{dT}{T} + R \cdot \frac{dV}{V} = 0$$

$$\text{If, in addition, } C_V \text{ is constant} \quad C_V \cdot \ln\left(\frac{T_2}{T_1}\right) + R \cdot \ln\left(\frac{V_2}{V_1}\right) = 0 \quad P_1 \cdot V_1^\gamma = P_2 \cdot V_2^\gamma$$

## SECOND LAW

Return to considerations of the general case (not necessarily an ideal gas).

Carnot (reversible) engine



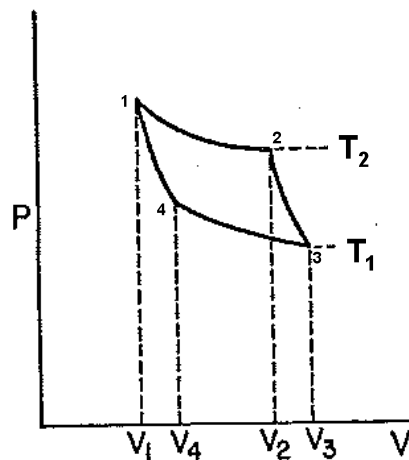
$$e = \text{efficiency} = \frac{W}{q_2} = \frac{q_2 - q_1}{q_2} = 1 - \frac{q_1}{q_2}$$

Consider two identical Carnot engines running in opposite directions. Unless they have same efficiency a perpetual motion can be built. Therefore,

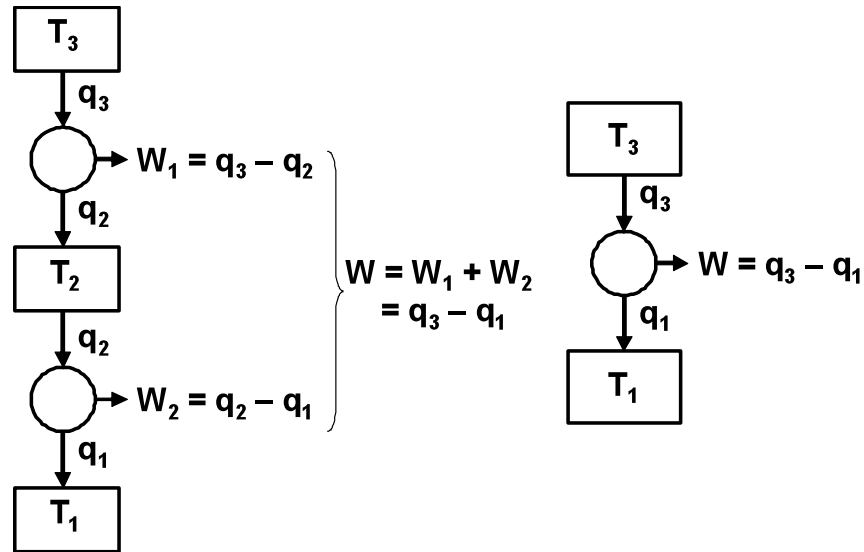
$$e = \bar{f}(T_1, T_2) \quad \frac{q_1}{q_2} = f(T_1, T_2)$$

For a general gas running to produce  $W > 0$

,



$P_1, V_1$  to  $P_2, V_2$  is a reversible isothermal expansion at temperature  $T_2$   
 $P_2, V_2$  to  $P_3, V_3$  is a reversible adiabatic expansion to temperature  $T_1$   
 $P_3, V_3$  to  $P_4, V_4$  is a reversible isothermal compression at temperature  $T_1$   
 $P_4, V_4$  to  $P_1, V_1$  is a reversible adiabatic compression to temperature  $T_2$



From left Carnot engines,

$$\frac{q_2}{q_3} = f(T_2, T_3)$$

$$\frac{q_1}{q_2} = f(T_1, T_2)$$

$$\frac{q_1}{q_3} = f(T_1, T_2) \cdot f(T_2, T_3)$$

From right Carnot engine,

$$\frac{q_1}{q_3} = f(T_1, T_3)$$

The two conditions are equivalent, therefore,

$$f(T_1, T_3) = f(T_1, T_2) \cdot f(T_2, T_3) \rightarrow f(T_1, T_2) = \frac{f(T_1, T_3)}{f(T_2, T_3)} = \frac{q_1}{q_2}$$

Note that  $f(T_1, T_2)$  is independent of  $T_3$  so that  $\rightarrow \frac{q_1}{q_2} = f(T_1, T_2) = \frac{F(T_1)}{G(T_2)}$

$$\text{Then } \frac{F(T_1)}{G(T_3)} = \frac{F(T_1)}{G(T_2)} \cdot \frac{F(T_2)}{G(T_3)} \rightarrow G(T_2) = F(T_2)$$

Now choose  $F(T) = T$  so that  $T$  is the thermodynamic temperature scale and,

$$\frac{q_1}{q_2} = f(T_1, T_2) = \frac{T_1}{T_2}$$

When the temperature is defined this way it is called Kelvin's thermodynamic temperature scale.

Before using the ideal gas law, it is necessary to check to see if the temperature in this law is consistent with the above definition of temperature. Therefore, return to the ideal gas law temporarily. Calculate  $W$  and  $q$  for each of the four parts of the Carnot cycle.

Isothermal expansion:  $W_1 = q_2 = R \cdot T_2 \cdot \ln\left(\frac{V_2}{V_1}\right)$

Adiabatic expansion:  $W_2 = \int_{T_1}^{T_2} C_V \cdot dT \quad q = 0$

Isothermal compression:  $W_3 = -q_1 = R \cdot T_1 \cdot \ln\left(\frac{V_4}{V_3}\right)$

Adiabatic compression:  $W_4 = -\int_{T_1}^{T_2} C_V \cdot dT \quad q = 0$

$$W = W_1 + W_2 + W_3 + W_4 = R \cdot T_2 \cdot \ln\left(\frac{V_2}{V_1}\right) + R \cdot T_1 \cdot \ln\left(\frac{V_4}{V_3}\right)$$

Using the thermodynamic temperature result,  $\frac{q_1}{q_2} = \frac{T_1}{T_2}$ , yields  $\frac{V_2}{V_1} = \frac{V_3}{V_4}$  so that,

$$W = R \cdot (T_2 - T_1) \cdot \ln\left(\frac{V_2}{V_1}\right) \text{ and then}$$

$$e = \text{efficiency} = \frac{W}{q_2} = \frac{T_2 - T_1}{T_2}$$

This result for efficiency is the same as the earlier definition so the temperature in the ideal gas law is on a thermodynamic temperature scale.

Returning now to the general case, a common definition for the Second Law of Thermodynamics is that for any reversible engine.

$$\oint \frac{dq}{T} \equiv \oint dS = 0 \text{ where } S \text{ is the entropy}$$

and for any engine that is not reversible,

$$\oint \frac{dq}{T} < 0 \quad \text{e. g.} \quad \frac{q_2}{T_2} - \frac{q_1}{T_1} < 0$$

The above equation is known as the Inequality of Clausius.

Return again to the ideal gas to determine some expressions for entropy.

$$dq = dE + P \cdot dV = C_V \cdot dT + \frac{R \cdot T}{V} \cdot dV$$

$$dS = \frac{dq}{T} = C_V \cdot \frac{dT}{T} + R \cdot \frac{dV}{V}$$

If  $C_V$  is constant,

$$S_2 - S_1 = C_V \cdot \ln\left(\frac{T_2}{T_1}\right) + R \cdot \ln\left(\frac{V_2}{V_1}\right)$$

If  $V$  is constant also,

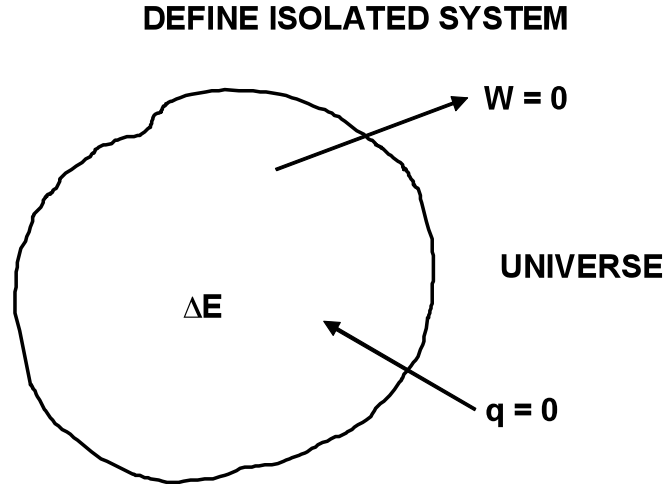
$$S_2 - S_1 = C_V \cdot \ln\left(\frac{T_2}{T_1}\right)$$

If, instead, the change is isothermal,

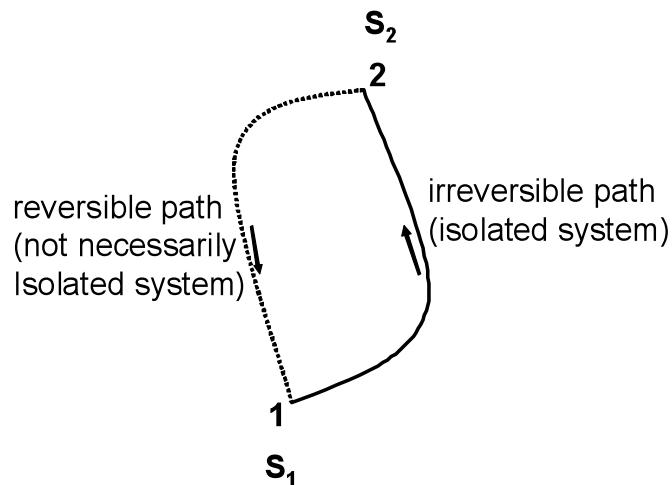
$$S_2 - S_1 = R \cdot \ln\left(\frac{V_2}{V_1}\right) = R \cdot \ln\left(\frac{P_1}{P_2}\right)$$

## EQUILIBRIUM CONSIDERATIONS

First, an isolated system is defined as having  $W = 0$  and  $q = 0$  as shown below.



Consider the following cycle for this isolated system.



For this cycle, recalling the Inequality of Clausius,

$$\int_{S_1}^{S_2} \frac{dq}{T} \Big|_{\text{IRREVERSIBLE}} + \int_{S_2}^{S_1} \frac{dq}{T} \Big|_{\text{REVERSIBLE}} < 0$$

The first integral must vanish since  $q = 0$ . The second integral equals  $S_1 - S_2$ . Therefore,

$$S_1 - S_2 < 0 \quad \text{or} \quad S_2 - S_1 > 0$$



This shows that, whereas the energy of the universe is constant, the entropy of the universe is approaching a maximum. An isolated system may also be defined as having  $E$  and  $V$  constant.

Consider a spontaneous change in an isolated system. It must be accompanied by  $\Delta S > 0$ .

Equilibrium is defined as the state where no spontaneous changes occur. From this two equivalent equilibrium criteria are deduced. They are,

- 1 At constant  $E$  and  $V$  the entropy is maximized.
- 2 At constant  $S$  and  $V$  the internal energy is minimized.

Although these are valid, they have limited use. The second criterion is applied for spring-mass systems in mechanics thus leading to the minimum energy theorem.

The above two equilibrium conditions are not too useful in chemistry. Now get two more equilibrium related results that are widely used. Let,

$A$  = work function or Helmholtz free energy =  $E - T \cdot S$

$F$  = thermodynamic potential = free energy = Gibbs free energy =  $H - T \cdot S$

$F = A + P \cdot V$

For a constant  $T$  reversible change,

$$\Delta A = \Delta E - T \cdot \Delta S \equiv -W_{\text{MAX}}$$

For a real system,

$$W < W_{\text{MAX}}$$

For a constant  $P$  reversible change,

$$\Delta F = \Delta A + P \cdot \Delta V$$

if this change is also a constant temperature change,

$$\Delta F = -W_{\text{MAX}} + P \cdot \Delta V \equiv -W_{\text{NET}}$$

Most laboratory experiments (electricity excluded) in chemistry are performed under conditions of constant  $T$  and  $P$  such that  $W_{\text{NET}} = 0$  so that  $\Delta F = 0$ . Since  $\Delta S > 0$  or  $\Delta H < 0$  cause  $\Delta F < 0$  another equilibrium condition is determined.

The two new equilibrium conditions are,

1. At constant  $T$  and  $P$ :  $F$  at equilibrium is a minimum
2. At constant  $T$  and  $V$ :  $A$  at equilibrium is a maximum

## DETERMINATION OF PROPERTIES FROM EXPERIMENTAL RESULTS

$$dF = dE + P \cdot dV + V \cdot dP - T \cdot dS - S \cdot dT$$

$$dE = T \cdot dS - P \cdot dV$$

so that,

$$dF = V \cdot dP - S \cdot dT$$

$$\therefore \left. \frac{\partial F}{\partial P} \right|_T = V \quad \text{and} \quad \left. \frac{\partial F}{\partial T} \right|_P = -S$$

For an isothermal change,  $\Delta F = F_2 - F_1 = \int_1^2 V \cdot dP$  so, given an equation of state, if  $F$  is known at one pressure it can be found for any other pressure. For the case of an ideal gas,  $\Delta F = R \cdot T \cdot \ln\left(\frac{P_2}{P_1}\right)$

For a change at constant pressure

$$\left. \frac{\partial F}{\partial T} \right|_P = -S = \frac{F - H}{T}$$

if, in addition, the change is at constant temperature,

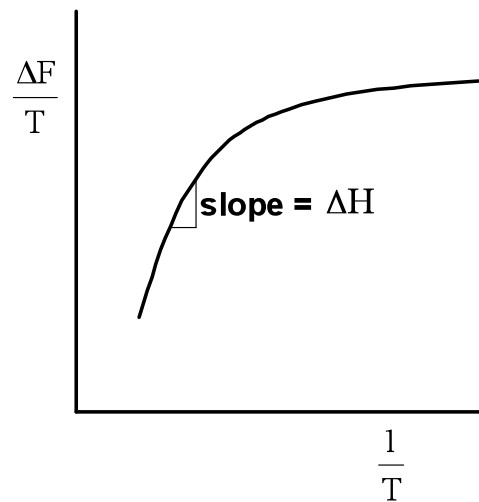
$$\left. \frac{\partial \Delta F}{\partial T} \right|_P = -\Delta S = \frac{\Delta F - \Delta H}{T}$$

this equation is called the Gibbs-Helmholtz equation and it may be converted to the form,

$$\frac{\partial \left( \frac{\Delta F}{T} \right)}{\partial \left( \frac{1}{T} \right)} \bigg|_P = \Delta H$$

Thus the slope of the plot of  $\frac{\Delta F}{T}$  versus  $\frac{1}{T}$  is equal to  $\Delta H$  as shown below.

curve measured for constant P



Other relations between the thermodynamic variables can be derived using the Gibbs free energy function,  $F$ . Consider the identity,

$$\frac{\partial}{\partial P} \left( \frac{\partial F}{\partial T} \right) \Big|_P = \frac{\partial}{\partial T} \left( \frac{\partial F}{\partial P} \right) \Big|_T$$

Since it has been shown that  $\frac{\partial F}{\partial P} \Big|_T = V$  and  $\frac{\partial F}{\partial T} \Big|_P = -S$  there results that,

$$\frac{\partial S}{\partial P} \Big|_T = - \frac{\partial V}{\partial T} \Big|_P$$

so at constant temperature,

$$\Delta S = - \int_{P_1}^{P_2} \frac{\partial V}{\partial T} \Big|_P \cdot dP = - \int_{P_1}^{P_2} \alpha \cdot V_O \cdot dP$$

This integration can be performed if the equation of state is known. In the case of an

ideal gas we already have shown that  $\Delta S = R \cdot \ln \left( \frac{V_2}{V_1} \right) = R \cdot \ln \left( \frac{P_1}{P_2} \right)$

At constant pressure,

$$dS = \frac{dq}{T} = \frac{dH}{T} = \frac{C_P \cdot dT}{T} \quad \rightarrow \quad \Delta S = \int_{T_1}^{T_2} \frac{C_P}{T} \cdot dT$$

At constant volume,

$$dS = \frac{dq}{T} = \frac{dE}{T} = \frac{C_V \cdot dT}{T} \quad \rightarrow \quad \Delta S = \int_{T_1}^{T_2} \frac{C_V}{T} \cdot dT$$

## SUMMARY OF THERMODYNAMIC VARIABLES

$$H = E + P \cdot V$$

Enthalpy

$$A = E - T \cdot S$$

Helmholtz free energy or work function

$$F = E + P \cdot V - T \cdot S$$

Gibbs free energy or thermodynamic potential

$$dE = T \cdot dS - P \cdot dV$$

$$dH = T \cdot dS + V \cdot dP$$

$$dA = -S \cdot dT - P \cdot dV$$

$$dF = -S \cdot dT + V \cdot dP$$

$$\left. \frac{\partial S}{\partial V} \right|_T = \left. \frac{\partial P}{\partial T} \right|_V$$

$$\left. \frac{\partial S}{\partial P} \right|_T = \left. \frac{\partial V}{\partial T} \right|_P$$

$$C_P = \left. \frac{dq}{dT} \right|_P = T \cdot \left. \frac{\partial S}{\partial T} \right|_P$$

$$C_V = \left. \frac{dq}{dT} \right|_V = T \cdot \left. \frac{\partial S}{\partial T} \right|_V$$

$$\left. \frac{\partial E}{\partial V} \right|_T + P = T \cdot \left. \frac{\partial P}{\partial T} \right|_V$$

$$\left. \frac{\partial H}{\partial P} \right|_T - V = -T \cdot \left. \frac{\partial V}{\partial T} \right|_P$$

$$\mu_{J.T.} = \left. \frac{\partial T}{\partial P} \right|_H = -\frac{1}{C_P} \cdot \left. \frac{\partial H}{\partial P} \right|_T = \frac{T \cdot \left. \frac{\partial V}{\partial T} \right|_P - V}{C_P}$$

$$\alpha = \frac{1}{V_O} \cdot \left. \frac{\partial V}{\partial T} \right|_P$$

## THERMODYNAMIC CONSIDERATIONS FOR MATERIALS

### INTRODUCTION

A requirement from physical science is that any theory must conform to the general results from Thermodynamics. The purpose of Section VI is to tie the results given above to Classical Thermodynamics and to determine any constraints that must be imposed on constitutive equations in order for them to conform to Classical Thermodynamics. A brief review of Classical Thermodynamics is in an appendix included at the end of this work.

In the case of a Continuum Mechanics formulation the system is a fixed mass particle so that the stresses and strains may be considered uniform. The first essential part of the Appendix concerns the First Law of Thermodynamics for fixed mass systems which is expressed as,

$$\dot{q} = \dot{E} + \dot{W}$$

where,

$$\begin{aligned}\dot{q} &= \text{time rate of heat flow into the system from its exterior} \\ &= T \cdot \dot{s} \text{ for a reversible process} \\ \dot{E} &= \text{time rate of change of internal energy} \\ \dot{W} &= \text{time rate of work being done by the system on its exterior}\end{aligned}$$

In addition, define,

$$\begin{aligned}T &= \text{absolute temperature} \\ \dot{s} &= \text{time rate of change of entropy} \\ \rho &= \text{mass density}\end{aligned}$$

When a specific constitutive equation is considered, it is often possible to determine  $\dot{W}$  explicitly. Substituting  $\dot{W}$  into the first law and solving for  $\dot{s}$  yields an equation whose validity must be determined. The condition that  $s$  be a perfect differential (i.e.  $s$  is a property dependent only on the state of the material) leads to a condition that must be satisfied by  $E$ . When this condition is satisfied then the Inequality of Clausius is valid and it becomes a way of expressing the Second Law of Thermodynamics as,

$$\oint \frac{dq}{T} = \oint ds \geq 0$$

where the inequality becomes the equality only for a reversible cycle.

A special, important result from Thermodynamics is that an equilibrium condition is defined. This is accomplished by considering an isolated system ( $\dot{q}$  and  $\dot{W}$  are both zero) and showing, based on the Inequality of Clausius, that any spontaneous change of the thermodynamic properties will result in an increase in entropy of the system. Equilibrium is defined as a stable state where no spontaneous change occurs in an isolated system and it implies that  $E$  will be a minimum in this state. For small deviations in the thermodynamic properties from the state being considered the conditions,

$$\delta E = 0 \quad \text{and} \quad \delta^2 E > 0$$

must be satisfied where  $\delta E$  and  $\delta^2 E$  are the first and second variations of  $E$ . It is noted that the usual stability calculations concerning buckling of beams and other structures is not covered by these considerations although the thermodynamic results can be extended to cover structural stability.

Several common, elementary, constitutive equations are reviewed in the section below. In each case, the expressions for  $E$  and  $\dot{s}$  are determined as well as investigating the conditions for an equilibrium state. In each case, the derivation is given in spatial coordinates. These reviews show the kind of restrictions thermodynamics imposes on constitutive equations.

## SELECTED, ILLUSTRATIVE, CONSTITUTIVE EQUATIONS

### LINEAR THERMOELASTICITY

The constitutive equation relates the strains,  $e_{ij}$ , stresses,  $s_{ij}$ , and absolute temperature,  $T$ , as,

$$\sigma_{ij} = \rho \cdot \hat{\lambda} \cdot (e_{kk} - 3 \cdot \alpha \cdot (T - T_O)) \cdot \delta_{ij} + 2 \cdot \rho \cdot \hat{G} \cdot (e_{ij} - \alpha \cdot (T - T_O) \cdot \delta_{ij})$$

where in terms of Young's modulus,  $\hat{E}$ , and Poisson's ratio,  $\nu$ ,

$$\rho \cdot \hat{\lambda} = \frac{\nu \cdot \hat{E}}{(1 + \nu) \cdot (1 - 2 \cdot \nu)}$$

$$\rho \cdot \hat{G} = \frac{\hat{E}}{2 \cdot (1 + \nu)}$$

and

$\alpha$  = thermal coefficient of linear expansion

$\rho$  = mass density, a function of  $e_{ij}$  and  $T$

$T_O$  = a constant reference temperature



The parameters  $\hat{\lambda}$ ,  $\hat{G}$  and  $\alpha$  are constants so that, up to this point,  $E$  and  $v$  are functions of  $e_{ij}$  and  $T$ .

The thermodynamic system under consideration is a particle whose mass is constant. The rate of work done by this particle is,

$$\dot{W} = - \frac{\sigma_{ij} \cdot \dot{e}_{ij}}{\rho}$$

Now assume the internal energy,  $E$ , is a function of  $e_{ij}$  and  $T$  so that,

$$\dot{E} = \frac{\partial E}{\partial e_{ij}} \cdot \dot{e}_{ij} + \frac{\partial E}{\partial T} \cdot \dot{T}$$

and the Thermodynamic First Law gives,

$$\dot{q} = \dot{E} + \dot{W} = \left( \frac{\partial E}{\partial e_{ij}} - \frac{\sigma_{ij}}{\rho} \right) \cdot \dot{e}_{ij} + \frac{\partial E}{\partial T} \cdot \dot{T}$$

The entropy production rate,  $\dot{s}$ , is,

$$\dot{s} = \frac{\dot{q}}{T} = \frac{1}{T} \cdot \left( \frac{\partial E}{\partial e_{ij}} - \frac{\sigma_{ij}}{\rho} \right) \cdot \dot{e}_{ij} + \frac{1}{T} \cdot \frac{\partial E}{\partial T} \cdot \dot{T}$$

In order that  $s$  be a state function, the following condition must be satisfied,

$$\frac{\partial}{\partial T} \left( \frac{1}{T} \cdot \left( \frac{\partial E}{\partial e_{ij}} - \frac{\sigma_{ij}}{\rho} \right) \right) = \frac{\partial}{\partial e_{ij}} \left( \frac{1}{T} \cdot \frac{\partial E}{\partial T} \right)$$

which gives,

$$\frac{\partial E}{\partial e_{ij}} = \frac{\sigma_{ij}}{\rho} - T \cdot \frac{\partial}{\partial T} \left( \frac{\sigma_{ij}}{\rho} \right)$$

When the thermoelasticity constitutive equation given above is substituted into this condition, the result is,

$$\frac{\partial E}{\partial e_{ij}} = \hat{\lambda} \cdot e_{kk} \cdot \delta_{ij} + 2 \cdot \hat{G} \cdot e_{ij} + \left( 3 \cdot \hat{\lambda} + 2 \cdot \hat{G} \right) \alpha \cdot T_O \cdot \delta_{ij}$$

Integration of  $\frac{\partial E}{\partial e_{ij}}$  gives,

$$E = \frac{1}{2} \cdot \hat{\lambda} \cdot (e_{kk})^2 + \hat{G} \cdot e_{ij} \cdot e_{ij} + (\hat{\beta} \cdot \hat{\lambda} + 2 \cdot \hat{G}) \alpha \cdot T_O \cdot e_{kk} + H(T)$$

then,

$$\dot{q} = (\hat{\beta} \cdot \hat{\lambda} + 2 \cdot \hat{G}) \alpha \cdot T \cdot \dot{e}_{kk} + \frac{\partial H(T)}{\partial T} \cdot \dot{T}$$

$$\dot{s} = (\hat{\beta} \cdot \hat{\lambda} + 2 \cdot \hat{G}) \alpha \cdot \dot{e}_{kk} + \frac{\partial H(T)}{\partial T} \cdot \frac{\dot{T}}{T}$$

In order to relate  $H(T)$  to a physically familiar quantity, note that  $T$  is an independent thermodynamic property and when the strain rates are zero the value of  $\dot{q}$  is,

$$\dot{q} \Big|_{\dot{e}_{ij}=0} = \frac{\partial H(T)}{\partial T} \cdot \dot{T} = c_v \cdot \dot{T}$$

where  $c_v$  is the specific heat at constant volume and assumed to be constant. Then.  $H(T)$  may be written as,

$$H(T) = c_v \cdot (T - T_1)$$

where  $T_1$  is a constant of integration. Consequently,  $E$  may be written as,

$$E = \frac{1}{2} \cdot \hat{\lambda} \cdot (e_{kk})^2 + \hat{G} \cdot e_{ij} \cdot e_{ij} + c_v \cdot (T - T_1)$$

and,

$$\dot{q} = (\hat{\beta} \cdot \hat{\lambda} + 2 \cdot \hat{G}) \alpha \cdot T \cdot \dot{e}_{kk} + c_v \cdot \dot{T}$$

$$\dot{s} = (\hat{\beta} \cdot \hat{\lambda} + 2 \cdot \hat{G}) \alpha \cdot \dot{e}_{kk} + c_v \cdot \frac{\dot{T}}{T}$$

In the case of linear thermoelasticity the constitutive equation is linearized with respect to the strains and the temperature. This process causes the value of  $\rho$  to be a constant in the constitutive equation and then  $\hat{E}$  and  $\nu$  are also constants in accordance with the usual thermoelastic theory.

When this constant mass thermoelastic system is isolated, the first variation of  $E$ ,  $\delta E$ , vanishes since  $\dot{E}$  vanishes and the second variation,  $\delta^2 E$ , is positive definite as the

quadratic quantity  $\frac{1}{2} \cdot \lambda \cdot (e_{kk})^2 + G \cdot e_{ij} \cdot e_{ij}$  is positive definite in  $e_{ij}$ . Consequently, the system is stable.

The temperature,  $T$ , is the absolute temperature in the above derivation. When the constitutive equation is used in problem solving, it is common to replace  $(T - T_0)$  with a temperature that is not a true thermodynamic temperature (e.g. degrees Celsius).

### LINEAR, VISCOUS, COMPRESSIBLE NEWTONIAN FLUID

The constitutive equation for this fluid may be written in terms of the stress,  $\sigma_{ij}$ , the strain,  $e_{ij}$ , the strain rate,  $\dot{e}_{ij}$ , and absolute temperature,  $T$ , in the form,

$$\sigma_{ij} = \rho \cdot \tilde{\lambda} \cdot \dot{e}_{kk} \cdot \delta_{ij} + 2 \cdot \rho \cdot \tilde{\mu} \cdot \dot{e}_{ij} + \rho \cdot \tilde{C} \cdot (e_{kk} - 3 \cdot \alpha \cdot (T - T_0)) \cdot \delta_{ij}$$

where,

$\tilde{\lambda}$ and $\tilde{\mu}$	= volumetric and shear viscosities, constant material properties
$\tilde{C}$	= elastic compressibility, constant material property
$\alpha$	= thermal coefficient of linear expansion, a constant
$\rho$	= mass density, a function of $e_{kk}$ and $T$
$T_0$	= a constant reference temperature

This case of a fluid introduces new considerations to the determination of the internal energy and the entropy functions. The presence of a viscosity implies that there is a dissipation of energy *within* the material element owing to flow. When the system is dissipative the entropy function cannot be derived using the constitutive equation in the same way as given in the case of the thermoelastic material. By assuming that  $E$  is a function of  $e_{ij}$ ,  $\dot{e}_{ij}$  and  $T$  and proceeding in same way as the thermoelastic material derivation shows there is no entropy function that is a state variable. When dissipation is present it is converted to heat and this must be reflected in the contributions to the first law. This may be accomplished in this case by splitting the stress into two parts,  $\sigma D_{ij}$  and  $\sigma S_{ij}$ . The stress,  $\sigma D_{ij}$ , is determined from the part of the constitutive equation causing dissipation while the stress,  $\sigma S_{ij}$ , is determined from the part of the constitutive equation contributing to the recoverable elastic strain energy as follows,

$$\sigma_{ij} = \sigma D_{ij} + \sigma S_{ij}$$

$$\sigma D_{ij} = \rho \cdot \tilde{\lambda} \cdot \dot{e}_{kk} \cdot \delta_{ij} + 2 \cdot \rho \cdot \tilde{\mu} \cdot \dot{e}_{ij}$$

$$\sigma S_{ij} = \rho \cdot \tilde{C} \cdot (e_{kk} - 3 \cdot \alpha \cdot T) \cdot \delta_{ij}$$

The rate of work being done by the system is  $-\frac{\sigma S_{ij} \cdot \dot{e}_{ij}}{\rho}$ . Assume the internal energy,  $E$ , is a function of  $e_{kk}$  and  $T$  so that the first law gives,

$$\dot{q} = \frac{\partial E}{\partial e_{kk}} \cdot \dot{e}_{kk} + \frac{\partial E}{\partial T} \cdot \dot{T} - \frac{\sigma S_{ij} \cdot \dot{e}_{ij}}{\rho} = \left( \frac{\partial E}{\partial e_{kk}} \cdot \delta_{ij} - \frac{\sigma S_{ij}}{\rho} \right) \cdot \dot{e}_{ij} + \frac{\partial E}{\partial T} \cdot \dot{T}$$

and the entropy production rate,  $\dot{s}$ , is

$$\dot{s} = \frac{1}{T} \cdot \left( \frac{\partial E}{\partial e_{kk}} \cdot \delta_{ij} - \frac{\sigma S_{ij}}{\rho} \right) \cdot \dot{e}_{ij} + \frac{\partial E}{\partial T} \cdot \frac{\dot{T}}{T}$$

In order for the entropy to be a state property,

$$-\frac{1}{T^2} \cdot \left( \frac{\partial E}{\partial e_{kk}} \cdot \delta_{ij} - \frac{\sigma S_{ij}}{\rho} \right) + \frac{1}{T} \cdot \left( \frac{\partial^2 E}{\partial T \partial e_{kk}} \cdot \delta_{ij} - \frac{\partial}{\partial T} \left( \frac{\sigma S_{ij}}{\rho} \right) \right) = \frac{1}{T} \cdot \frac{\partial^2 E}{\partial e_{ij} \partial T} = \frac{1}{T} \cdot \frac{\partial^2 E}{\partial e_{kk} \partial T} \cdot \delta_{ij}$$

Assuming the order of differentiation for the second derivatives are interchangeable, the equation becomes,

$$T \cdot \frac{\partial}{\partial T} \left( \frac{\sigma S_{ij}}{\rho} \right) - \frac{\sigma S_{ij}}{\rho} = - \frac{\partial E}{\partial e_{kk}} \cdot \delta_{ij}$$

When the constitutive equation for  $\sigma S_{ij}$  is substituted into the above equation, the result is,

$$\frac{\partial E}{\partial e_{kk}} = \tilde{C} \cdot (e_{kk} + 3 \cdot \alpha \cdot T_O)$$

The last equation is integrated to give,

$$E = \tilde{C} \cdot \left( \frac{1}{2} \cdot e_{kk}^2 + 3 \cdot \alpha \cdot T_O \cdot e_{kk} \right) + J(T)$$

where  $J(T)$  is an arbitrary function of  $T$ . When  $E$  is substituted into the expressions for heat flow rate and entropy production rate given above, the expressions become,

$$\dot{q} = 3 \cdot \alpha \cdot T \cdot \tilde{C} \cdot \dot{e}_{kk} + \frac{dJ(T)}{dT} \cdot \dot{T}$$

$$\dot{s} = 3 \cdot \alpha \cdot \tilde{C} \cdot \dot{e}_{kk} + \frac{dJ(T)}{dT} \cdot \frac{\dot{T}}{T}$$

When  $\dot{e}_{kk} = 0$ , the heat flow rate is usually written as  $c_v \cdot \dot{T}$  with  $c_v$  being the specific heat. In this case,

$$\frac{dJ(T)}{dT} = c_v$$

When  $c_v$  is a constant, integration yields,

$$J(T) = c_v \cdot (T - T_1)$$

where  $T_1$  is a constant of integration. To summarize,

$$\dot{q} = 3 \cdot \alpha \cdot T \cdot \vec{C} \cdot \dot{e}_{kk} + c_v \cdot \dot{T}$$

$$\dot{s} = 3 \cdot \alpha \cdot \vec{C} \cdot \dot{e}_{kk} + c_v \cdot \frac{\dot{T}}{T}$$

$$E = \frac{1}{2} \cdot \vec{E} \cdot e_{kk}^2 + 3 \cdot \vec{C} \cdot \alpha \cdot T_O \cdot e_{kk} + c_v \cdot (T - T_1)$$

The value of  $\dot{q}$  in these equations is the total heat flow rate for the system and some is generated internally while the remainder is supplied externally to the material element. The internal heat flow rate,  $\dot{q}_D$ , is,

$$\dot{q}_D = \frac{\sigma_{D_{ij}} \cdot \dot{e}_{ij}}{\rho} = \left( \tilde{\lambda} \cdot \dot{e}_{kk} \cdot \delta_{ij} + 2 \cdot \tilde{\mu} \cdot \dot{e}_{ij} \right) \dot{e}_{ij}$$

Now let the externally supplied heat flow rate be  $\dot{\hat{q}}$  so that,

$$\dot{q} = \dot{\hat{q}} + \dot{q}_D$$

and,

$$\dot{\hat{q}} = 3 \cdot \alpha \cdot T \cdot \vec{C} \cdot \dot{e}_{kk} + c_v \cdot \dot{T} - \bar{\lambda} \cdot \dot{e}_{kk}^2 - 2 \cdot \bar{\mu} \cdot \dot{e}_{ij} \cdot \dot{e}_{ij}$$

#### ELASTIC, PERFECTLY-PLASTIC SOLID

The formulation investigated here is the one appearing in the text, *Theory of Perfectly Plastic Solids*, by William Prager and Philip Hodge, Jr. (John Wiley & Sons, Inc., 1951). The von Mises stress,  $\sigma_{VM}$ , is defined to be,

$$\sigma_{VM} = \sqrt{\frac{3}{2} \cdot \sigma_{ij} \cdot \sigma_{ij} - \frac{1}{2} \cdot \sigma_{kk}^2}$$

and possible stress states must be such that,

$$\sigma_{VM} \leq \sigma_{YP}$$

where  $\sigma_{YP}$  is the yield point of the material, a constant. The strain is split into two parts. The elastic strain,  $eE_{ij}$ , is directly related to the stress state while the plastic strain,  $eP_{ij}$ , is adjusted to be proportional to the reduced stress,  $\sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk} \cdot \delta_{ij}$ . The total strain rate is the sum of the elastic strain rate and the plastic strain rate,  $\dot{e}E_{ij} + \dot{e}P_{ij}$ . The relationship between the stress and the elastic strain is,

$$\sigma_{ij} = \left( \rho \cdot \tilde{\lambda} \cdot eE_{kk} - \left( \beta \cdot \rho \cdot \tilde{\lambda} + 2 \cdot \rho \cdot \tilde{G} \right) \alpha \cdot T \right) \delta_{ij} + 2 \cdot \rho \cdot \tilde{G} \cdot eE_{ij}$$

where the material parameter nomenclature is the same nomenclature used for the elastic material considered above. The plastic strain changes over a loading increment when  $\sigma_{VM} = \sigma_{YP}$  during the increment. This change is expressed by,

$$\dot{e}P_{ij} = \Gamma \cdot \left( \sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk} \cdot \delta_{ij} \right) \quad \text{while } \sigma_{VM} = \sigma_{YP}$$

$$\dot{e}P_{ij} = 0 \quad \text{otherwise}$$

where  $\Gamma$  must be adjusted so that  $\sigma_{VM} = \sigma_{YP}$ . Note that  $\dot{e}P_{kk} = 0$  so that the plastic strains cause no rate of volume change. The rate of doing external work for the elastic strain is assumed to be recoverable while the rate of doing work for the plastic strain is assumed to be dissipated into a heat flow rate within the material element. Define these as,

$$\dot{W}_E = - \frac{\sigma_{ij} \cdot \dot{e}E_{ij}}{\rho} = - \left( \tilde{\lambda} \cdot eE_{kk} - \left( \beta \cdot \tilde{\lambda} + 2 \cdot \tilde{G} \right) \alpha \cdot T \right) \dot{e}E_{kk} - 2 \cdot \tilde{G} \cdot eE_{ij} \cdot \dot{e}E_{ij}$$

$$\dot{W}_P = - \frac{\sigma_{ij} \cdot \dot{e}P_{ij}}{\rho} = - 2 \cdot \tilde{G} \cdot eE_{ij} \cdot \Gamma \cdot \left( \sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk} \cdot \delta_{ij} \right) \quad \text{while } \sigma_{VM} = \sigma_{YP}$$

$$\dot{W}_P = 0 \quad \text{otherwise}$$

Now assume that the internal energy,  $E$ , is a function of the elastic strain,  $eE_{ij}$ , and the temperature  $T$ . For this material the first law is written as,

$$\dot{q} = \dot{E} + \dot{W}_E$$

so that,

$$\dot{q} = \left( \frac{\partial E}{\partial eE_{ij}} - (\tilde{\lambda} \cdot eE_{kk} - (\beta \cdot \tilde{\lambda} + 2 \cdot \tilde{G}) \alpha \cdot T) \delta_{ij} - 2 \cdot \tilde{G} \cdot eE_{ij} \right) \cdot \dot{eE}_{ij} + \frac{\partial E}{\partial T} \cdot \dot{T}$$

and,

$$\dot{s} = \frac{1}{T} \cdot \left( \frac{\partial E}{\partial eE_{ij}} - (\tilde{\lambda} \cdot eE_{kk} - (\beta \cdot \tilde{\lambda} + 2 \cdot \tilde{G}) \alpha \cdot T) \delta_{ij} - 2 \cdot \tilde{G} \cdot eE_{ij} \right) \cdot \dot{eE}_{ij} + \frac{1}{T} \cdot \frac{\partial E}{\partial T} \cdot \dot{T}$$

In order for the entropy to be a property,

$$\begin{aligned} & -\frac{1}{T^2} \cdot \left( \frac{\partial E}{\partial eE_{ij}} - (\tilde{\lambda} \cdot eE_{kk} - (\beta \cdot \tilde{\lambda} + 2 \cdot \tilde{G}) \alpha \cdot T) \delta_{ij} - 2 \cdot \tilde{G} \cdot eE_{ij} \right) + \frac{1}{T} \cdot \left( \frac{\partial^2 E}{\partial T \partial eE_{ij}} + (\beta \cdot \tilde{\lambda} + 2 \cdot \tilde{G}) \alpha \cdot \delta_{ij} \right) \\ & = \frac{1}{T} \cdot \frac{\partial^2 E}{\partial eE_{ij} \partial T} \end{aligned}$$

As usual, the order of differentiation of the second derivatives is assumed interchangeable so that,

$$\frac{\partial E}{\partial eE_{ij}} = \tilde{\lambda} \cdot eE_{kk} \cdot \delta_{ij} + 2 \cdot \tilde{G} \cdot eE_{ij}$$

When this equation is integrated there results,

$$E = \frac{1}{2} \cdot \tilde{\lambda} \cdot eE_{kk}^2 + \tilde{G} \cdot eE_{ij} \cdot eE_{ij} + K(T)$$

and,

$$\dot{q} = (\beta \cdot \tilde{\lambda} + 2 \cdot \tilde{G}) \alpha \cdot T \cdot \dot{eE}_{kk} + \frac{dK(T)}{dT} \cdot \dot{T}$$

$$\dot{s} = (\beta \cdot \tilde{\lambda} + 2 \cdot \tilde{G}) \alpha \cdot \dot{eE}_{kk} + \frac{1}{T} \cdot \frac{\partial K(T)}{\partial T} \cdot \dot{T}$$

Now define a specific heat at constant volume,  $c_v$ , using,

$$\dot{q} \Big|_{\dot{eE}_{kk}} = c_v \cdot \dot{T}$$

to obtain,

$$c_v = \frac{dK(T)}{dT}$$

where, obviously,  $c_V$  is a function of temperature only. The heat flow rate and entropy production rate may be written as,

$$\dot{q} = (\beta \cdot \tilde{\lambda} + 2 \cdot \tilde{G}) \alpha \cdot T \cdot \dot{E}_{kk} + c_V \cdot \dot{T}$$

$$\dot{s} = (\beta \cdot \tilde{\lambda} + 2 \cdot \tilde{G}) \alpha \cdot \dot{E}_{kk} + \frac{1}{T} \cdot c_V \cdot \dot{T}$$

Similar to the case for a fluid, the quantity  $\dot{q}$  is the total heat flow rate in the material element. The quantity  $\dot{W}_p$  is the rate of work for the plastic strain that is converted to a heat flow rate. Let  $\dot{\bar{q}}$  be the externally supplied heat flow rate so that,

$$\dot{\bar{q}} = \dot{q} - \dot{W}_p = (\beta \cdot \tilde{\lambda} + 2 \cdot \tilde{G}) \alpha \cdot T \cdot \dot{E}_{kk} + c_V \cdot \dot{T} + 4 \cdot \rho \cdot \tilde{G}^2 \cdot \Gamma \cdot \left( \mathbf{e}E_{ij} \cdot \mathbf{e}E_{ij} - \frac{1}{3} \cdot \mathbf{e}E_{kk}^2 \right)$$

#### INCOMPRESSIBLE BINGHAM MATERIAL.

The most common formulation neglects thermal expansion and elastic behavior of the material and this approximation is employed here. This material has a yield point stress that must be exceeded before the material can deform. When the yield stress is exceeded, the material flows similar to a fluid but with the flow rate proportional to the excess of the stress over the yield point stress. Let,

$$\sigma_{VM} = \sqrt{\frac{3}{2} \cdot \sigma_{ij} \cdot \sigma_{ij} - \frac{1}{2} \cdot \sigma_{kk}^2} = \sqrt{\frac{3}{2}} \cdot \sqrt{\sigma_{ij} \cdot \sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk}^2} = \sqrt{3} \cdot \tau_{VM}$$

where  $\sigma_{VM}$  is the von Mises stress in tension and  $\tau_{VM}$  is the von Mises stress in shear. The yield point stress in shear is denoted by  $\tau_{YP}$  and it is the value of the von Mises stress in simple shear that causes yielding of the material. For this material it is common to formulate the constitutive equation in terms of the constant value of  $\tau_{YP}$ . The constitutive equation for the incompressible Bingham material is.

$$\begin{aligned} 2 \cdot \mu \cdot \dot{e}_{ij} &= \frac{\sigma_{VM} - \sqrt{3} \cdot \tau_{YP}}{\sigma_{VM}} \cdot \left( \sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk} \cdot \delta_{ij} \right) && \text{when } \sigma_{VM} \geq \sqrt{3} \cdot \tau_{YP} \\ 2 \cdot \mu \cdot \dot{e}_{ij} &= 0 && \text{otherwise} \end{aligned}$$

When this material undergoes deformation, the entire rate of work done by the stresses is converted to a heat flow rate. Consequently, in the first law  $\dot{W} = 0$ . In addition, the internal energy is assumed to be a function of temperature only. Under these conditions, the first law becomes,

$$\dot{q} = \frac{\partial E}{\partial T} \cdot \dot{T}$$



and the entropy production rate is,

$$\dot{s} = \frac{\partial E}{\partial T} \cdot \frac{\dot{T}}{T}$$

Clearly,  $\frac{\partial E}{\partial T}$  may be interpreted as the specific heat at constant volume,  $c_v$ , so that,

$$\dot{q} = c_v \cdot \dot{T}$$

$$\dot{s} = c_v \cdot \frac{\dot{T}}{T}$$

During deformation, the quantity  $-\frac{\sigma_{ij} \cdot \dot{e}_{ij}}{\rho}$  is the heat flow rate internal to the material element and,

$$\frac{\sigma_{ij} \cdot \dot{e}_{ij}}{\rho} = \frac{\sigma_{VM} - \sqrt{3} \cdot \tau_{YP}}{2 \cdot \rho \cdot \mu \cdot \sigma_{VM}} \cdot \left( \sigma_{ij} \cdot \sigma_{ij} - \frac{1}{3} \cdot \sigma_{kk}^2 \right) = \frac{(\sigma_{VM} - \sqrt{3} \cdot \tau_{YP}) \sigma_{VM}}{3 \cdot \rho \cdot \mu}, \quad \sigma_{VM} \geq \sqrt{3} \cdot \tau_{YP}$$

so that the externally supplied heat flow rate,  $\dot{\hat{q}}$ , is,

$$\dot{\hat{q}} = c_v \cdot \dot{T} + \frac{(\sigma_{VM} - \sqrt{3} \cdot \tau_{YP}) \sigma_{VM}}{3 \cdot \rho \cdot \mu}, \quad \sigma_{VM} \geq \sqrt{3} \cdot \tau_{YP}$$

$$\dot{\hat{q}} = c_v \cdot \dot{T}, \quad \text{otherwise}$$

Owing to the assumption of incompressibility the mean stress,  $\frac{1}{3} \cdot \sigma_{kk}$ , is indeterminate from the deformation. A similar situation occurs in the case of any incompressible material..

## PENG-ROBINSON CUBIC EQUATION OF STATE

This equation is used frequently to represent the state of the material in vapor-liquid equilibrium calculations. For a specified state (vapor or liquid) the equation contains three constants,  $R$ ,  $a$  and  $b$ . It relates the pressure,  $p$ , to the specific volume,  $v$ , and temperature,  $T$ , as follows,

$$p = \frac{R \cdot T}{v - b} - \frac{a}{v^2 + 2 \cdot b \cdot v - b^2}$$

For this case assume the internal energy is a function of the specific volume and the temperature,  $E = E(v, T)$ . The first law yields,

$$\dot{q} = \left( \frac{\partial E}{\partial v} + p \right) \cdot \dot{v} + \frac{\partial E}{\partial T} \cdot \dot{T}$$

and then,

$$\dot{s} = \frac{\dot{q}}{T} = \frac{1}{T} \cdot \left( \frac{\partial E}{\partial v} + p \right) \cdot \dot{v} + \frac{\partial E}{\partial T} \cdot \frac{\dot{T}}{T}$$

In order for the entropy to be a state variable,

$$\frac{-1}{T^2} \cdot \left( \frac{\partial E}{\partial v} + p \right) + \frac{1}{T} \cdot \left( \frac{\partial^2 E}{\partial T \partial v} + \frac{\partial p}{\partial T} \right) = \frac{1}{T} \cdot \frac{\partial^2 E}{\partial v \partial T}$$

Assuming the second derivatives are independent of the order of differentiation gives,

$$\frac{\partial E}{\partial v} + p - T \cdot \frac{\partial p}{\partial T} = 0$$

When  $p$  is eliminated from this equation using the equation of state, the result is,

$$\frac{\partial E}{\partial v} = \frac{a}{v^2 + 2 \cdot b \cdot v - b^2}$$

and integration gives,

$$E = \frac{a}{\sqrt{8 \cdot b^2}} \cdot \ln \left( \frac{2 \cdot v + 2 \cdot b - \sqrt{8 \cdot b^2}}{2 \cdot v + 2 \cdot b + \sqrt{8 \cdot b^2}} \right) + L(T)$$

so that

$$\dot{q} = \frac{R \cdot T}{v - b} \cdot \dot{v} + \frac{dL(T)}{dT} \cdot \dot{T}$$

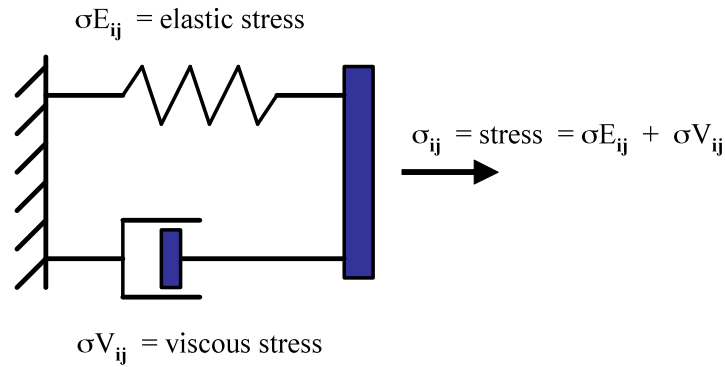
The multiplier of  $\dot{T}$  is the specific heat at constant volume,  $c_v$ , so the heat flow rate and entropy production rate become,

$$\dot{q} = \frac{R \cdot T}{v - b} \cdot \dot{v} + c_v \cdot \dot{T}$$

$$\dot{s} = \frac{\dot{q}}{T} = \frac{R}{v - b} \cdot \dot{v} + c_v \cdot \frac{\dot{T}}{T}$$

### VOIGT MATERIAL (KELVIN-VOIGT MATERIAL)

The sketch below is a conceptual description of this material. Although it is helpful to represent the physical characteristics of the material with this sort of sketch, D. C. Drucker (Second-order Effects in Elasticity. Plasticity and Fluid Dynamics, International Symposium, Haifa, Israel, April 23-27, 1962) has pointed out the limitations of such sketches.



The contributions to the stress,  $\sigma E_{ij}$ , and  $\sigma V_{ij}$ , are taken as the classical formulations for thermoelastic and viscous materials. The external work is associated with  $\sigma E_{ij}$  only as the work associated with  $\sigma V_{ij}$  is dissipated as heat in the material element. The total stress is the sum of the two contributions so,

$$\sigma E_{ij} = \rho \cdot \lambda \cdot (e_{kk} - 3 \cdot \alpha \cdot T) \cdot \delta_{ij} + 2 \cdot \rho \cdot G \cdot (e_{ij} - \alpha \cdot T \cdot \delta_{ij})$$

$$\sigma V_{ij} = \rho \cdot \bar{\lambda} \cdot \dot{e}_{kk} \cdot \delta_{ij} + 2 \cdot \rho \cdot \bar{\mu} \cdot \dot{e}_{ij}$$

$$\sigma_{ij} = \sigma E_{ij} + \sigma V_{ij}$$

The internal energy,  $E$ , is assumed to be a function of  $\sigma E_{ij}$  and  $T$  only. The work term is taken as  $-\frac{\sigma E_{ij} \cdot \dot{e}_{ij}}{\rho}$  and then the first law becomes.

$$\dot{q} = \left( \frac{\partial E}{\partial e_{ij}} - \frac{\sigma E_{ij}}{\rho} \right) \cdot \dot{e}_{ij} + \frac{\partial E}{\partial T} \cdot \dot{T}$$

and

$$\dot{s} = \frac{\dot{q}}{T} = \frac{1}{T} \cdot \left( \frac{\partial E}{\partial e_{ij}} - \frac{\sigma E_{ij}}{\rho} \right) \cdot \dot{e}_{ij} + \frac{\partial E}{\partial T} \cdot \frac{\dot{T}}{T}$$

The condition that must be satisfied in order that the entropy,  $s$ , be a state variable is,

$$\frac{-1}{T^2} \cdot \left( \frac{\partial E}{\partial e_{ij}} + \frac{\sigma E_{ij}}{\rho} \right) + \frac{1}{T} \cdot \left( \frac{\partial^2 E}{\partial T \partial e_{ij}} + \frac{\partial}{\partial T} \left( \frac{\sigma E_{ij}}{\rho} \right) \right) = \frac{1}{T} \cdot \frac{\partial^2 E}{\partial e_{ij} \partial T}$$

Assuming the order of differentiation for the second derivatives may be interchanged, this condition becomes,

$$\frac{\partial E}{\partial e_{ij}} = \frac{\sigma E_{ij}}{\rho} - T \cdot \frac{\partial}{\partial T} \left( \frac{\sigma E_{ij}}{\rho} \right)$$

When the constitutive equation is substituted into this condition, the result is,

$$\frac{\partial E}{\partial e_{ij}} = \lambda \cdot e_{kk} \cdot \delta_{ij} + 2 \cdot G \cdot e_{ij}$$

and integration gives,

$$E = \frac{1}{2} \cdot \lambda \cdot e_{kk}^2 + G \cdot e_{ij} \cdot e_{ij} + M(T)$$

with  $M(T)$  being an arbitrary function of temperature. Recognizing that the specific heat at constant volume,  $c_v$ , is related to  $M(T)$  through,

$$\frac{dM(T)}{dT} = c_v$$

yields,

$$\dot{q} = (3 \cdot \lambda + 2 \cdot G) \cdot \alpha \cdot T \cdot \dot{e}_{kk} + c_v \cdot \dot{T}$$

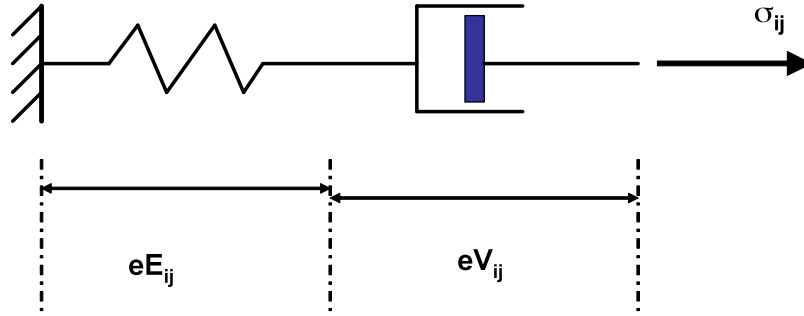
$$\dot{s} = (3 \cdot \lambda + 2 \cdot G) \cdot \alpha \cdot \dot{e}_{kk} + c_v \cdot \frac{\dot{T}}{T}$$

Since the internally generated heat flow rate is  $-\frac{\sigma V_{ij} \cdot \dot{e}_{ij}}{\rho}$ , the external heat flow rate,  $\hat{q}$ , is given by,

$$\begin{aligned}\dot{\bar{q}} &= \dot{q} + \frac{\sigma V_{ij} \cdot \dot{e}_{ij}}{\rho} = \dot{q} + \bar{\lambda} \cdot \dot{e}_{kk}^2 + 2 \cdot \bar{\mu} \cdot \dot{e}_{ij} \cdot \dot{e}_{ij} \\ &= (3 \cdot \lambda + 2 \cdot G) \cdot \alpha \cdot T \cdot \dot{e}_{kk} + c_v \cdot \dot{T} + \bar{\lambda} \cdot \dot{e}_{kk}^2 + 2 \cdot \bar{\mu} \cdot \dot{e}_{ij} \cdot \dot{e}_{ij}\end{aligned}$$

## MAXWELL MATERIAL

The sketch below gives a conceptual, physical understanding of the Maxwell material. The strain has separate elastic and viscous components,  $eE_{ij}$  and  $eV_{ij}$ , that are induced by the total stress,  $\sigma_{ij}$ .



The analytical model developed here uses classical definitions to relate  $\sigma_{ij}$ ,  $eE_{ij}$  and  $eV_{ij}$  as follows,

$$\sigma_{ij} = \rho \cdot \lambda \cdot (eE_{kk} - 3 \cdot \alpha \cdot T) \cdot \delta_{ij} + 2 \cdot \rho \cdot G \cdot (eE_{ij} - \alpha \cdot T \cdot \delta_{ij})$$

$$\sigma_{ij} = \rho \cdot \bar{\lambda} \cdot \dot{e}V_{kk} \cdot \delta_{ij} + 2 \cdot \rho \cdot \bar{\mu} \cdot \dot{e}V_{ij}$$

and the total strain rate,  $\dot{e}_{ij}$ , is defined as,

$$\dot{e}_{ij} = \dot{e}E_{ij} + \dot{e}V_{ij}$$

The external rate of work is  $-\frac{\sigma_{ij} \cdot \dot{e}E_{ij}}{\rho}$  while the internal rate of work that is converted

to heat flow rate is  $-\frac{\sigma_{ij} \cdot \dot{e}V_{ij}}{\rho}$  and the internal energy,  $E$ , is assumed to be a function of  $eE_{ij}$  and  $T$  only. The first law is,

$$\dot{q} = \left( \frac{\partial E}{\partial eE_{ij}} - \frac{\sigma_{ij}}{\rho} \right) \cdot \dot{e}E_{ij} + \frac{\partial E}{\partial T} \cdot \dot{T}$$

and

$$\dot{s} = \frac{\dot{q}}{T} = \frac{1}{T} \cdot \left( \frac{\partial E}{\partial eE_{ij}} - \frac{\sigma_{ij}}{\rho} \right) \cdot \dot{e}E_{ij} + \frac{\partial E}{\partial T} \cdot \frac{\dot{T}}{T}$$

The condition that entropy be a state variable is,

$$-\frac{1}{T^2} \cdot \left( \frac{\partial E}{\partial eE_{ij}} - \frac{\sigma_{ij}}{\rho} \right) + \frac{1}{T} \cdot \left( \frac{\partial^2 E}{\partial T \partial eE_{ij}} - \frac{\partial}{\partial T} \left( \frac{\sigma_{ij}}{\rho} \right) \right) = \frac{1}{T} \cdot \frac{\partial^2 E}{\partial eE_{ij} \partial T}$$

With the assumption that the order of differentiation may be interchanged, this equation becomes,

$$\frac{\partial E}{\partial eE_{ij}} = \frac{\sigma_{ij}}{\rho} - \frac{\partial}{\partial T} \left( \frac{\sigma_{ij}}{\rho} \right)$$

Substitution of the constitutive equation into this equation gives,

$$\frac{\partial E}{\partial eE_{ij}} = \lambda \cdot eE_{kk} \cdot \delta_{ij} + 2 \cdot G \cdot eE_{ij}$$

and integration leads to,

$$E = \frac{1}{2} \cdot \lambda \cdot eE_{kk}^2 + G \cdot eE_{ij} \cdot eE_{ij} + N(T)$$

The function of integration,  $N(T)$ , is related to the specific heat at constant volume,  $c_v$ , through,

$$c_v = \frac{dN(T)}{dT}$$

so that,

$$\dot{q} = (3 \cdot \lambda + 2 \cdot \mu) \cdot \alpha \cdot T \cdot \dot{e}E_{kk} + c_v \cdot \dot{T}$$

$$\dot{s} = (3 \cdot \lambda + 2 \cdot \mu) \cdot \alpha \cdot \dot{e}E_{kk} + c_v \cdot \frac{\dot{T}}{T}$$

The external heat flow rate,  $\dot{\bar{q}}$ , is the difference between the total heat flow rate,  $\dot{q}$ , and the internal heat flow rate,  $-\frac{\sigma_{ij} \cdot \dot{e}E_{ij}}{\rho}$ , so that,

$$\begin{aligned}
\dot{\hat{q}} &= \dot{q} + \frac{\sigma_{ij} \cdot \dot{e}V_{ij}}{\rho} = \dot{q} + \bar{\lambda} \cdot \dot{e}V_{kk}^2 + 2 \cdot \bar{\mu} \cdot \dot{e}V_{ij} \cdot \dot{e}V_{ij} \\
&= (3 \cdot \lambda + 2 \cdot \mu) \cdot \alpha \cdot T \cdot \dot{e}E_{kk} + c_v \cdot \dot{T} + \bar{\lambda} \cdot \dot{e}V_{kk}^2 + 2 \cdot \bar{\mu} \cdot \dot{e}V_{ij} \cdot \dot{e}V_{ij}
\end{aligned}$$

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