

# Thermodynamic Equations of State

- Thermodynamic equations of state will lead to an understanding of concepts such as surface tension, etc.
- Leads to a knowledge of how to predict the physical property or at least relations between physical properties.

## Fundamentals of Thermodynamics:

- Variables in the lab:  $P, V, T$
- First law:  $dE = dw + dq$
- Energy is state function; any combination of heat and work possible
- Microscopic scale: energy is sum of rotational, vibrational, translational and electronic energy levels.
- Remember  $w = -PdV$ ; negative sign indicates system energy increases when work done on system.
- Assume only  $PdV$  work and defining entropy as
$$dq_{rev}/T \equiv dS$$
- Leads to first law:  $dE = -PdV + TdS$
- Gibbs Free Energy:  $G = H - TS$
- Helmholtz Energy:  $F = E - TS$

# Relationship between E and Volume in terms of P, V, T

- Take partial of First Law:  $dE = -PdV + TdS$  with respect to V at constant T:

$$\left(\frac{\partial E}{\partial V}\right)_T = -P + T\left(\frac{\partial S}{\partial V}\right)_T$$

- Equations should be expressed in terms of P, V, T.

- Helmholz free energy:**  $F \equiv E - TS$

- Differentiate:  $dF \equiv dE - TdS - SdT$

- Substitute from first law.  $dF \equiv -PdV + TdS - TdS - SdT$

- Total Differential of F:  $dF = \left(\frac{\partial F}{\partial V}\right)_T dV + \left(\frac{\partial F}{\partial T}\right)_V dT$

- Comparing leads to:  $\left(\frac{\partial F}{\partial V}\right)_T = -P + \left(\frac{\partial^2 F}{\partial V \partial T}\right) = -\left(\frac{\partial P}{\partial T}\right)_V$

- And also:  $\left(\frac{\partial F}{\partial T}\right)_V = -S + \left(\frac{\partial^2 F}{\partial T \partial V}\right) = -\left(\frac{\partial S}{\partial V}\right)_T$

- But:  $\left(\frac{\partial^2 F}{\partial T \partial V}\right) = \left(\frac{\partial^2 F}{\partial V \partial T}\right)$

- Substituting from previous two equations:  $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

- Which is leads to:  $\boxed{\left(\frac{\partial E}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V}$

# Pressure Dependence of Enthalpy

- Enthalpy is defined in terms of energy, pressure and volume:  $H \equiv E + PV$ .
- Differentiating:  $dH = dE + PdV + VdP$ .
- From the first law:  $dE = -PdV + TdS$ ;
- Substituting:  $dH = PdV + VdP - PdV + TdS$   
 $= VdP + TdS$
- Divide by  $dP$  and hold  $T$  constant:  $\left(\frac{\partial H}{\partial P}\right)_T = V + T\left(\frac{\partial S}{\partial P}\right)_T$

- Use Gibbs Free Energy:  $G = H - TS$  or  
 $dG = dH - TdS - SdT$
- Substitute for  $dH$ :  $dG = VdP + TdS - TdS - SdT = VdP - SdT$
- Write total differential for free energy,  $G(T,P)$ :

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

- By inspection:  $\left(\frac{\partial G}{\partial P}\right)_T = V$  and  $\left(\frac{\partial G}{\partial T}\right)_P = -S$
- Second derivative:  $\left(\frac{\partial^2 G}{\partial P \partial T}\right) = \left(\frac{\partial V}{\partial T}\right)_P$  and  $\left(\frac{\partial^2 G}{\partial T \partial P}\right) = -\left(\frac{\partial S}{\partial P}\right)_T$
- Or:  $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$
- Substitute for enthalpy equation:  $\boxed{\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P}$

# Equations of State: Temperature Dependence

- Recall 3 variables to be used are P, V, T.
- Knowledge of two of the variables allows determination of the energy state of the system.
- Two polynomial equations of state used here.
  - $V = f(P)$  and
  - $P = f(V)$
- $V = V_o[1 + a_o(T) - a_1(T)P + a_2(T)P^2 + \dots]$  where
  - coefficients  $a_j$  are functions of temperature.
  - $V_o$  = volume at absolute zero.

- Differentiate with respect to T and neglect higher terms:

$$\left(\frac{\partial V}{\partial T}\right)_P = V_o \left(\frac{\partial a_o}{\partial T}\right)_P$$

- When using only the first two terms of the series expansion, we have:  $V = V_o[1 + a_o(T)]$ .
- Substitute for  $V_o$ :  $V_o = V/[1+a_o(T)]$ .

$$\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{[1+a_o(T)]} \left(\frac{\partial a_o}{\partial T}\right)_P$$

- When  $a_o \ll 1$ , the equations reduces to:

$$\boxed{\left(\frac{\partial a_o}{\partial T}\right)_P = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = a}$$

where  $a = \text{volume expansivity}$ , relative change in volume with temperature; related to temperature variation of  $a_o$ .

# Equations of State: Pressure Dependence

- Found by taking derivative of equation of state with respect to pressure:

$$\left(\frac{\partial V}{\partial P}\right)_T = -V_0 a_1 \quad \vee \quad -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T = \frac{V_0}{V} a_1$$

where higher pressure terms are ignored (only first order considered significant).

- But  $V = V_0[1 + a_0]$ ; so that

$$\chi = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T = \frac{a_1}{1 + a_0} \approx a_1$$

since  $a_1 \ll a_0 \ll 1$

- $c =$  ***isothermal compressibility***.
- Pressure as a function of T, V:

$$P = P_0(T) + P_1(T) \left[ \frac{V_0 - V}{V_0} \right] + P_2(T) \left[ \frac{V_0 - V}{V_0} \right]^2 + \dots$$

- $P_i =$  material dependent coefficients; determined experimentally.
- $P_0 =$  pressure required to decrease the volume of the solid at higher temperature to what it would be at 0 K and no pressure.
- $P_0 \ll P_1$  or  $P_2$

## Relationship between $P_i$ and $a_i$

- Recall:  $V = V_0[1 + a_0(T) - a_1(T)P + a_2(T)P^2 + \dots]$
- Solve for Volume:  $\frac{V}{V_0} = 1 + a_0(T) - a_1(T)P + a_2(T)P^2$ 

$$\frac{V}{V_0} - 1 = a_0(T) - a_1(T)P + a_2(T)P^2$$

$$\frac{V_0 - V}{V_0} = -a_0(T) + a_1(T)P - a_2(T)P^2$$
- We use this in the earlier equation:
 
$$P = P_0(T) + P_1(T)\left[\frac{V_0 - V}{V_0}\right] + P_2(T)\left[\frac{V_0 - V}{V_0}\right]^2 + \dots$$
- To get  $P = P_0(T) + P_1(T)(-a_0(T) + a_1P - a_2P^2 + \dots) + P_2(T)(-a_0(T) + a_1P - a_2P^2 + \dots)^2 + \dots$
- Expand the second term
- Neglect squared and higher terms in terms of  $a_0$  and  $P_0$ .  $P = P_0 + P_1(-a_0 + a_1P - a_2P^2 + \dots) + P_2(-2a_0a_1P + a_0a_2P^2 + a_1^2P^2 + \dots)^2 + \dots$
- This can only be true when the following happens:
 
$$P_0 - P_1a_0 = 0,$$

$$P_1a_1 - 2P_2a_0a_1 = 1,$$

$$-P_1a_2 + 2P_2a_0a_2 + P_2a_1^2 = 0$$

## Relationship between $P_i$ and $a_i$ (cont.)

- Solve for  $a_i$  from
 
$$P_o - P_1 a_o = 0,$$

$$P_1 a_1 - 2P_2 a_o a_1 = 1,$$

$$- P_1 a_2 + 2P_2 a_o a_2 + P_2 a_1^2 = 0$$

- Gives:

$$a_o = \frac{P_o}{P_1},$$

$$a_1 = \frac{1}{P_1 - 2P_2 a_o} = \frac{1}{P_1} \left( 1 + \frac{2P_o P_2}{P_1^2} \right)$$

$$a_2 = \frac{P_2}{P_1^3} \left( 1 + \frac{6P_o P_2}{P_1^2} \right)$$

- $P_i$  can also be expressed in terms of  $a_i$ ,
- Figure shows that compressibility increases with atomic number.
- Slopes at high pressures are similar for all.
- Coefficients of expansion nearly constant at absolute zero (see figure), but increase at higher temperatures .

# Pressure Dependence of Heat Capacity

- Recall the definition of heat capacity:  $C_P = \left(\frac{\partial H}{\partial T}\right)_P$

- Take its derivative with respect to P at constant T

$$\left(\frac{\partial C_P}{\partial P}\right)_T = \frac{\partial}{\partial P} \left[ \left(\frac{\partial H}{\partial T}\right)_P \right]_T = \frac{\partial}{\partial T} \left[ \left(\frac{\partial H}{\partial P}\right)_T \right]_P$$

- But earlier we showed:  $\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$

- Substitute:  $\left(\frac{\partial C_P}{\partial P}\right)_T = \frac{\partial}{\partial P} \left[ \left(\frac{\partial H}{\partial T}\right)_P \right]_T = \frac{\partial}{\partial T} \left[ V - T\left(\frac{\partial V}{\partial T}\right)_P \right]_P$
- $$= \left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial T}{\partial T}\right)_P \left(\frac{\partial V}{\partial T}\right)_P - T \left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

- We can now use the equation of state to determine an equation for calculating heat capacity under various conditions.

- Recall:  $V = V_o [1 + a_o(T) - a_1(T)P + a_2(T)P^2 + \dots]$

- Substitute:

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -TV_o \left( \frac{\partial^2 [1 + a_o(T) + a_1(T)P + a_2(T)P^2]}{\partial T^2} \right)_P$$

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -TV_o \left( \frac{\partial^2 a_o(T)}{\partial T^2} + \frac{\partial^2 a_1(T)}{\partial T^2} P + \frac{\partial^2 a_2(T)}{\partial T^2} P^2 \right)_P$$



## C<sub>P</sub> Vs P(cont)

- Integration gives the pressure dependence of C<sub>P</sub>.

$$\int_{C_P^o}^{C_P} \partial C_P = -TV_o \int_0^P \left( \frac{\partial^2 a_o(T)}{\partial T^2} + \frac{\partial^2 a_1(T)}{\partial T^2} P + \frac{\partial^2 a_2(T)}{\partial T^2} P^2 \right) dP$$

$$C_P = C_P^o - TV \left( \frac{\partial^2 a_o(T)}{\partial T^2} P + \frac{1}{2} \frac{\partial^2 a_1(T)}{\partial T^2} P^2 + \frac{1}{3} \frac{\partial^2 a_2(T)}{\partial T^2} P^3 \right)$$

- C<sub>P</sub><sup>o</sup> = heat capacity at zero pressure.
- The first second derivative term is dominant at high temperature and heat capacity is expected to decrease with increasing pressure in this temperature regime (see negative sign in equation).
- Recall that alpha is the volume expansivity:  $\alpha = \left( \frac{\partial a_o}{\partial T} \right)_P$
- The first term is the temperature coefficient of thermal expansion.
- This term nearly linear at high temperatures.

## C<sub>V</sub> vs P

- Earlier we showed: 
$$\left(\frac{\partial E}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V$$

- Take derivative of both sides with respect to T:

$$\frac{\partial^2 E}{\partial T \partial V} = \frac{\partial^2 E}{\partial V \partial T} = -\frac{\partial P}{\partial T} + \frac{\partial T}{\partial T} \frac{\partial P}{\partial T} + T \frac{\partial^2 P}{\partial T^2}$$

- But: 
$$C_V = \left(\frac{\partial E}{\partial T}\right)_V$$

- Substitute: 
$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \frac{\partial^2 P}{\partial T^2}$$

- Earlier we used the equation of state:

$$P = P_0(T) + P_1(T) \left[ \frac{V_0 - V}{V_0} \right] + P_2(T) \left[ \frac{V_0 - V}{V_0} \right]^2 + \dots$$

- Take second derivative:

$$\frac{\partial^2 P}{\partial T^2} = \frac{\partial P_0^2(T)}{\partial T^2} + \frac{\partial P_2^2(T)}{\partial T^2} \left[ \frac{V_0 - V}{V_0} \right] + \frac{\partial P_0^2(T)}{\partial T^2} \left[ \frac{V_0 - V}{V_0} \right]^2 + \dots$$

- Substitute into above equation, rearrange, and

integrate: 
$$\int_{C_V^o}^{C_V} \partial C_V = T \int_{V_0}^V \frac{\partial^2 P}{\partial T^2} \partial V$$

$$\int_{C_V^o}^{C_V} \partial C_V = T \int_{V_0}^V \left( \frac{\partial P_0^2(T)}{\partial T^2} + \frac{\partial P_2^2(T)}{\partial T^2} \left[ \frac{V_0 - V}{V_0} \right] + \frac{\partial P_0^2(T)}{\partial T^2} \left[ \frac{V_0 - V}{V_0} \right]^2 + \dots \right) dV$$

## C<sub>V</sub> vs P(cont)

- But  $d\left(\frac{V_o - V}{V_o}\right) = -\frac{dV}{V_o}$  so that

$$\int_{C_V^o}^{C_V} \partial C_V = -V_o T \int_{V_o}^V \left( \frac{\partial P_0^2(T)}{\partial T^2} + \frac{\partial P_1^2(T)}{\partial T^2} \left[ \frac{V_o - V}{V_o} \right] + \frac{\partial P_2^2(T)}{\partial T^2} \left[ \frac{V_o - V}{V_o} \right]^2 + \dots \right) d\left(\frac{V_o - V}{V_o}\right)$$

which becomes:

$$C_V = C_V^o - V_o T \left( \frac{\partial P_0^2(T)}{\partial T^2} \left[ \frac{V_o - V}{V_o} \right] + \frac{1}{2} \frac{\partial P_1^2(T)}{\partial T^2} \left[ \frac{V_o - V}{V_o} \right]^2 + \frac{1}{3} \frac{\partial P_2^2(T)}{\partial T^2} \left[ \frac{V_o - V}{V_o} \right]^3 + \dots \right)$$

- Theoretical calculations using heat capacity can be done with constant volume;
- Experimental evaluation of heat capacities are usually at constant pressure.
- A relationship between the two needed.
- The total derivatives for S(T,V) and S(T,P) multiplied by T are:

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

- First term first reaction: C<sub>P</sub>dT
- First term second reaction: C<sub>V</sub>dT
- We also note the following Maxwell reactions:

$$\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \quad \wedge \quad \left( \frac{\partial S}{\partial P} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_P$$

- Substitute into above equations and subtract from each other to get:

$$(C_P - C_V) dT = T \left( \frac{\partial P}{\partial T} \right)_V dV - T \left( \frac{\partial V}{\partial T} \right)_P dP$$

## C<sub>V</sub> vs P(cont2)

- At either constant volume or temperature we get:

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

- We now find the two partials using the equations of state:

$$\left( \frac{\partial P}{\partial T} \right)_V = \left( \frac{\partial P_o}{\partial T} \right)_V + \left( \frac{\partial P_1}{\partial T} \right)_V \left[ \frac{V_o - V}{V_o} \right] - P_1 d \left( \frac{V}{V_o} \right)_T + \dots$$

- Assume:  $V = V_o$  and third term is zero since it is at constant volume:

$$\left( \frac{\partial P}{\partial T} \right)_V \approx \left( \frac{\partial(a_o/a_1)}{\partial T} \right) = \frac{a}{a_1}$$

- Taking the derivative at constant pressure of the other equation of state to obtain the other partial:

$$\begin{aligned} \left( \frac{\partial V}{\partial T} \right)_P &= V_o \left( \frac{\partial \left( 1 + a_o(T) - a_1(T)P + a_2(T)P^2 \right)}{\partial T} \right)_P \\ &= \left( \frac{\partial a_o(T)}{\partial T} - \frac{\partial a_1(T)}{\partial T} P + \frac{\partial a_2(T)}{\partial T} P^2 \right)_P = \left( \frac{\partial a_o(T)}{\partial T} \right)_{P=0} \end{aligned}$$

- Substitute into equation at top of page to get:

$$\begin{aligned} C_P^o - C_V^o &= \frac{TV_o a^2}{a_1} \\ &= \frac{TV_o a^2}{c} \end{aligned}$$

which allows us to determine one heat capacity for the other, if molar volume and  $\alpha$  is known.

## S, E, G vs P

- Pressure's effect on these variables determined as we did with heat capacity.

- For **Entropy** recall that:  $S = \int_0^T \frac{C_V}{T} dT$

- Substitute for  $C_V$  from earlier relationships:

$$\begin{aligned}
 S &= \int_0^T \frac{C_V}{T} dT = \\
 &= \int_0^T \frac{C_V^o}{T} dT - V_o \int_0^T \left( \frac{\partial P_0^2(T)}{\partial T^2} \left[ \frac{V_o - V}{V_o} \right] + \frac{1}{2} \frac{\partial P_1^2(T)}{\partial T^2} \left[ \frac{V_o - V}{V_o} \right]^2 + \frac{1}{3} \frac{\partial P_2^2(T)}{\partial T^2} \left[ \frac{V_o - V}{V_o} \right]^3 + \dots \right) dT \\
 &= C_V^o \ln T - V_o \left( \frac{\partial P_0(T)}{\partial T} \left[ \frac{V_o - V}{V_o} \right] + \frac{1}{2} \frac{\partial P_1(T)}{\partial T} \left[ \frac{V_o - V}{V_o} \right]^2 + \frac{1}{3} \frac{\partial P_2(T)}{\partial T} \left[ \frac{V_o - V}{V_o} \right]^3 + \dots \right)
 \end{aligned}$$

- Energy is determined from the relationship we developed earlier:

$$\left( \frac{\partial E}{\partial V} \right)_T = -P + T \left( \frac{\partial P}{\partial T} \right)_V$$

- We use the equation of state to determine an expression for this:

$$T \left( \frac{\partial P}{\partial T} \right)_V - P =$$

$$\left[ T \left( \frac{\partial P_o}{\partial T} \right)_V - P_o \right] + \left[ T \left( \frac{\partial P_1}{\partial T} \right)_V - P_1 \right] \left[ \frac{V_o - V}{V_o} \right] + \left[ T \left( \frac{\partial P_2}{\partial T} \right)_V - P_2 \right] \left[ \frac{V_o - V}{V_o} \right]^2 + \dots$$

## S, E, G vs P(cont)

- Now we rearrange and integrate:

$$\int_{E_o}^E dE = E - E_o =$$

$$-V_o \int \left\{ \left[ T \left( \frac{\partial P_o}{\partial T} \right)_V - P_o \right] + \left[ T \left( \frac{\partial P_1}{\partial T} \right)_V - P_1 \right] \left[ \frac{V_o - V}{V_o} \right] + \left[ T \left( \frac{\partial P_2}{\partial T} \right)_V - P_2 \right] \left[ \frac{V_o - V}{V_o} \right]^2 + \dots \right\} d \left( \frac{V_o - V}{V_o} \right)$$

$$E = E_{oo} - V_o \left[ T \left( \frac{\partial P_o}{\partial T} \right)_V - P_o \right] \left[ \frac{V_o - V}{V_o} \right] + \frac{1}{2} \left[ T \left( \frac{\partial P_1}{\partial T} \right)_V - P_1 \right] \left[ \frac{V_o - V}{V_o} \right] + \frac{1}{3} \left[ T \left( \frac{\partial P_2}{\partial T} \right)_V - P_2 \right] \left[ \frac{V_o - V}{V_o} \right]^2$$

- Free Energy,  $G = f(P, V, T)$ :  $dG = -SdT + VdP$ .

- Replace each term

$$\int_{G_{oo}}^G dG = -\int_0^T \left( S_o + \int_0^T C_{v_o} d \ln T \right) dT + \int_0^P V_o \left[ 1 + a_o + a_1 P + a_2 P^2 \right] dP$$

$$G = E_{oo} - \int_0^T \left( \int_0^T C_{v_o} d \ln T \right) dT + PV_o \left[ 1 + a_o + \frac{1}{2} a_1 P + \frac{1}{3} a_2 P^2 \right]$$

- Equations of state used with standard thermodynamic relationships to determine values of thermodynamic quantities from a set of data.

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