

1. LiH melts at 961.8 K and 1 bar with an enthalpy of fusion of 22.6 kJ mol<sup>-1</sup>. The heat capacities of the solid and liquid are  $C_{pm}(s) = 62.6 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $C_{pm}(l) = 68.0 \text{ J K}^{-1} \text{ mol}^{-1}$ . Calculate  $q$ ,  $w$ ,  $\Delta H$ ,  $\Delta U$ ,  $\Delta S$  for the reversible heating of one mole of LiH from 900 to 1000 K. Why is one of these five quantities negligibly small (*i.e.* zero within the precision of the calculations)?

2. a) The change in the internal energy of any closed system is the sum of the heat absorbed by the system and the work done on the system:  $dU = dq + dw$ . Combine this First Law expression for  $dU$  with the Second Law to derive the **fundamental equation of thermodynamics**

[4]

$$dU = TdS - pdV$$

[Hint: Any path can be used to calculate  $dU$  (*why?*). Take a convenient reversible path!]

- b) Use  $dU = TdS - pdV$  and the definition of the Helmholtz energy ( $A = U - TS$ ) to derive

$$dA = -SdT - pdV$$

- c) Why are  $T$  and  $V$  sometimes called the “natural” variables for the Helmholtz energy?

3. Use the differential  $dG = -SdT + Vdp$  of the Gibbs energy to prove:

[3]

$$\text{a) } (\partial G/\partial T)_p = -S \qquad \text{b) } (\partial G/\partial p)_T = V \qquad \text{c) } (\partial V/\partial T)_p = -(\partial S/\partial p)_T$$

4. Calcium carbonate ( $\text{CaCO}_3$ , 100.1 g mol<sup>-1</sup>) is found in nature in two different crystalline forms: aragonite (mined in Aragon, a province of Spain) and calcite.

[6]

Data at 25 °C and 1 bar:

	aragonite	calcite
$\Delta H_{fm}^\circ/(\text{kJ mol}^{-1})$	-1207.13	-1206.92
$S_m^\circ/(\text{J K}^{-1} \text{ mol}^{-1})$	88.7	92.9
density/(g cm <sup>-3</sup> )	2.93	2.71

- a) Which form of calcium carbonate is stable at 25 °C and 1 bar? Justify your answer.

- b) At what pressure would the two forms of calcium carbonate be in equilibrium at 25 °C?

[Hint: Use  $(\partial G/\partial p)_T = V$  to calculate  $(\partial \Delta G/\partial p)_T = \Delta V$ .]

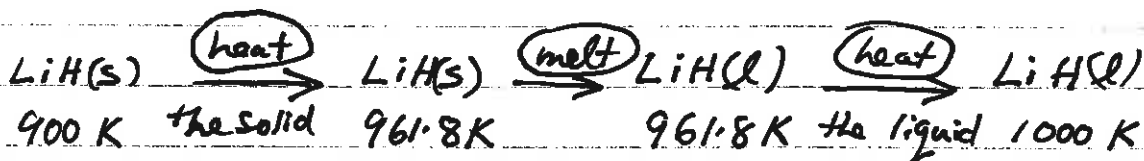
- c) At what pressure would the two forms of calcium carbonate be in equilibrium at 500 °C?

[Hint: Use  $(\partial G/\partial T)_p = -S$  to calculate  $(\partial \Delta G/\partial T)_p = -\Delta S$ .]

5. Relate  $(\partial S/\partial V)_T$  to quantities “easily” measured in terms of  $p$ ,  $T$  and  $V$ . (Hint: A partial derivative with respect to volume at constant temperature suggests looking at the Maxwell relation for the Helmholtz energy, whose natural variables are  $T$  and  $V$ .)

[2]

1. Heat LiH from 900 K to 1000 K at 1 bar.



$$q = \int_{900\text{K}}^{961.8\text{K}} C_{pm}^{\circ}(\text{s}) dT + \Delta H_{\text{fus,m}}^{\circ} + \int_{961.8\text{K}}^{1000\text{K}} C_{pm}^{\circ}(\text{l}) dT$$

$$= 62.6 (961.8 - 900) + 22,600 + 68.0 (1000 - 961.8)$$

$$= 3869 + 22,600 + 2598$$

$q = 29,067 \text{ J}$   
 $= \Delta H$  (constant pressure)

$\Delta V$  is small, probably  $< 1 \text{ cm}^3$  (solid and liquid)

$$w = - \int_{V_i}^{V_f} p_{\text{ext}} dV = - p \int_{V_i}^{V_f} dV = - p \Delta V$$

w order of magnitude  $\sim (1 \text{ bar})(1 \text{ cm}^3) \approx (10^5 \text{ Pa})(10^{-6} \text{ m}^3)$   
 $\sim 0.1 \text{ J}$  negligible

$w = 0$

$\Delta U = q + w = q = 29,067 \text{ J}$

$$\Delta S = \int_{900\text{K}}^{961.8\text{K}} \frac{C_{pm}^{\circ}(\text{s})}{T} dT + \frac{\Delta H_{\text{fus,m}}^{\circ}}{T_{\text{fus}}} + \int_{961.8\text{K}}^{1000\text{K}} \frac{C_{pm}^{\circ}(\text{l})}{T} dT$$

melting, the major source of  $\Delta S$

$$= C_{pm}^{\circ}(\text{s}) \ln\left(\frac{961.8}{900}\right) + \frac{22600}{961.8} + C_{pm}^{\circ}(\text{l}) \ln\left(\frac{1000}{961.8}\right)$$

$$= 4.15 + 23.50 + 2.65 = 30.30 \text{ J K}^{-1}$$

2. a) reversible path =

$$dS = \frac{dq_{rev}}{T}$$

$$P = P_{ext} \quad dw = -P_{ext} dV$$

$$dq_{rev} = T dS$$

$$dw_{rev} = -p dV$$

$$dU = dq_{rev} + dw_{rev}$$

$$dU = T dS - p dV$$

b)  $dA = d(U - TS)$

$$= dU - d(TS)$$

$$= dU - T dS - S dT$$

$$= \cancel{T dS} - p dV - \cancel{T dS} - S dT$$

$$dA = -S dT - p dV = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV$$

use the "chain" rule  
 $d(TS) = T dS + S dT$

c) the differentials of  $T$  and  $V$  are in the expression for  $dA$  and

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

$$\left(\frac{\partial A}{\partial V}\right)_T = -p$$

3.

$$G(T, P)$$

$$dG = \left( \frac{\partial G}{\partial T} \right)_P dT + \left( \frac{\partial G}{\partial P} \right)_T dP \quad \text{eq. 1}$$

$$\text{compare: } dG = -SdT + VdP \quad \text{eq. 2}$$

$T$  and  $P$  are independent variables

eq. 1 and eq. 2 provide

$$\text{a) } \left( \frac{\partial G}{\partial T} \right)_P = -S \quad \text{b) } \left( \frac{\partial G}{\partial P} \right)_T = V$$

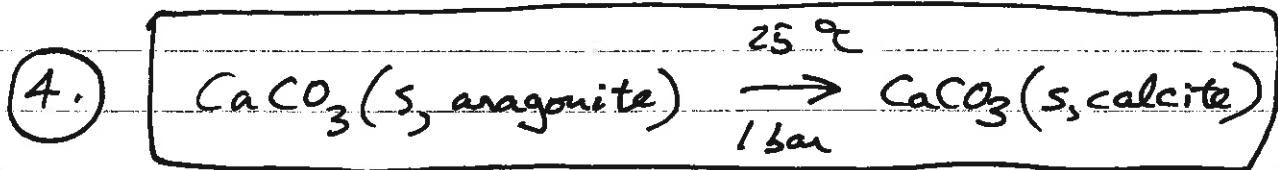
$$\text{c) } \left[ \frac{\partial}{\partial P} \left( \frac{\partial G}{\partial T} \right)_P \right]_T = \left[ \frac{\partial}{\partial T} \left( \frac{\partial G}{\partial P} \right)_T \right]_P$$

-S      from a) and b)      V

Why? Because  $dG$  is an exact differential and the function  $G(T, P)$  exists and can be differentiated

$$\left[ \frac{\partial}{\partial P} (-S) \right]_T = \left[ \frac{\partial}{\partial T} V \right]_P$$

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



$$\begin{aligned} \Delta H^\circ &= \Delta H_{\text{fm}}^\circ(\text{calcite}) - \Delta H_{\text{fm}}^\circ(\text{aragonite}) \\ &= -1206.92 - (-1207.13) = 0.21 \text{ kJ} \\ &= 210 \text{ J (small!)} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ &= S_m^\circ(\text{calcite}) - S_m^\circ(\text{aragonite}) \\ &= 92.9 - 88.7 \text{ J K}^{-1} \\ &= 4.2 \text{ J K}^{-1} \end{aligned}$$

at fixed temperature and pressure (25°C, 1 bar here), the convenient criterion for a spontaneous process is

$$\Delta G_{T,P} < 0$$

$$\Delta G = \Delta(U + PV - TS) = \Delta(H - TS)$$

$$\Delta G_{T,P} = \Delta(\overbrace{H-TS}^{\text{fixed}}) = \Delta H - T\Delta S$$

at 1 bar ( $P^\circ$ ):  $\Delta H^\circ = +210 \text{ J}$  (unfavorable for a spont. process)  
 $\Delta S^\circ = +4.2 \text{ J K}^{-1}$  (favorable!)

$$\Delta G_T^\circ = \Delta H^\circ - T\Delta S^\circ$$

Who wins?  $\Delta H^\circ$  or  $-T\Delta S^\circ$ ?

The suspense mounts!

Note: No mixing here. Pure aragonite  $\rightarrow$  pure calcite

$$\Delta G_{298.15\text{K}}^\circ = (210 \text{ J}) - (298.15 \text{ K})(4.2 \text{ J K}^{-1})$$

Spontaneous reaction

$$= 210 - 1252 \text{ J}$$

$$\Delta G_{298.15\text{K}}^\circ = -1042 \text{ J}$$

for aragonite  $\rightarrow$  calcite

more stable

(4. cont.)

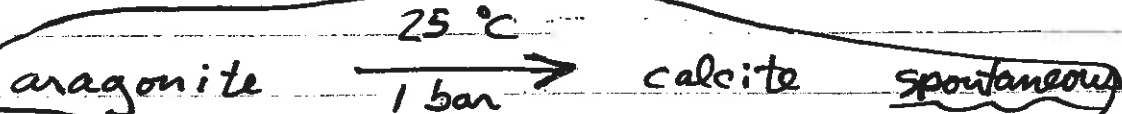
we:

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

and

$$V = \frac{\text{mass}}{\text{density}}$$

b)



but aragonite is denser,  $\therefore$  favored at high pressure

$$\Delta G^\circ_{298.15\text{K}} = -1042 \text{ J}$$

Spontaneous forward reaction at  $25^\circ \text{C}$ , 1 bar

$$\Delta G = G_m(\text{calcite}) - G_m(\text{aragonite})$$

take the pressure derivative

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \left(\frac{\partial G_m(\text{calcite})}{\partial P}\right)_T - \left(\frac{\partial G_m(\text{aragonite})}{\partial P}\right)_T$$

$$= V_m(\text{calcite}) - V_m(\text{aragonite})$$

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V = \frac{M_{\text{calcite}}}{\rho_{\text{calcite}}} - \frac{M_{\text{aragonite}}}{\rho_{\text{aragonite}}}$$

$$= \frac{100.1 \text{ g mol}^{-1}}{2.71 \text{ g cm}^{-3}} - \frac{100.1 \text{ g mol}^{-1}}{2.93 \text{ g cm}^{-3}}$$

aragonite  $\xrightleftharpoons[p]{25^\circ \text{C}}$  calcite in equilibrium when  $\Delta G = 0$

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V = 36.94 - 34.16 = 2.78 \frac{\text{cm}^3}{\text{mol}} = \boxed{2.78 \times 10^{-6} \frac{\text{m}^3}{\text{mol}}}$$

notice:  $\Delta G$  increases with pressure, aragonite (denser, smaller volume) eventually is stable

$$\Delta G_P = \Delta G_{P^0} + \int_{P^0}^P \left(\frac{\partial G}{\partial P}\right)_T dp = \Delta G_{P^0} + \int_{P^0}^P \Delta V dp$$

$$\Delta G_P = \Delta G_{P^0} + \Delta V(P - P^0)$$

at equilibrium at P  $\Delta G_P = 0$

$$0 = -1042 \text{ J} + (2.78 \times 10^{-6}) (P - P^0)$$

$$P - P^0 = 3.75 \times 10^8 \text{ Pa} = 3750 \text{ bar}$$

$$\boxed{P \approx 3750 \text{ bar}}$$

(4 cont.) use  $\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S$   $\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V$

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

$$d\Delta G = \left(\frac{\partial \Delta G}{\partial T}\right)_P dT + \left(\frac{\partial \Delta G}{\partial P}\right)_T dP = -\Delta S dT + \Delta V dP$$

$\Delta G = -1042 \text{ J}$  at  $298 \text{ K}$  and  $1 \text{ bar}$

$\Delta G = 0$  (for equilibrium) at  $500 \text{ }^\circ\text{C}$  and pressure  $P$  ( $773 \text{ K}$ )

$$\Delta G_{773\text{K}, P} = 0$$

$$\Delta G_{298\text{K}, 1\text{bar}} = -1042 \text{ J}$$

$$\Delta G_{773\text{K}, P} - \Delta G_{298\text{K}, 1\text{bar}} = \left(\frac{\partial \Delta G}{\partial T}\right)_P (773\text{K} - 298\text{K}) + \left(\frac{\partial \Delta G}{\partial P}\right)_T (P - P^\circ)$$

$$0 - (-1042 \text{ J}) = (-\Delta S) (475 \text{ K}) + \Delta V (P - 10^5 \text{ Pa})$$

$$1042 \text{ J} = (-4.2 \text{ J K}^{-1}) (475 \text{ K}) + (2.78 \times 10^{-6} \text{ m}^3) (P - 10^5 \text{ Pa})$$

$$P - 10^5 \text{ Pa} = \frac{3037 \text{ J}}{2.78 \times 10^{-6} \text{ m}^3} = 1.09 \times 10^9 \text{ Pa}$$

$$P = 1.09 \times 10^9 + 10^5 \text{ Pa}$$

$$P = 1.09 \times 10^9 \text{ Pa} = \boxed{10900 \text{ bar}}$$

$$(5.) \left( \frac{\partial s}{\partial v} \right)_T ?$$

suggests  
 $v, T$  independent variables  
and  $A(T, v)$

$$dA = -s dT - p dv$$
$$\left[ \frac{\partial}{\partial v} \left( \frac{\partial A}{\partial T} \right)_v \right]_T = \left[ \frac{\partial}{\partial T} \left( \frac{\partial A}{\partial v} \right)_T \right]_v$$

$dA$  is an exact  
differential of the  
state function  $A(T, v)$

$$\left[ \frac{\partial}{\partial v} (-s) \right]_T = \left[ \frac{\partial}{\partial T} (-p) \right]_v$$

$$\boxed{\left( \frac{\partial s}{\partial v} \right)_T = \left( \frac{\partial p}{\partial T} \right)_v}$$

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

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

$$= \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_p$$
$$- \frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_T$$

$$\boxed{\left( \frac{\partial s}{\partial v} \right)_T = \frac{\beta}{\kappa}}$$