Chemistry 231 **Assignment #7** (due Tuesday 10 November, in class)

1. [5] LiH melts at 961.8 K and 1 bar with an enthalpy of fusion of 22.6 kJ mol^{-1}. The heat capacities of the solid and liquid are $C_{pm}(s) = 62.6\ J\ K^{-1}\ mol^{-1}$ and $C_{pm}(l) = 68.0\ J\ K^{-1}\ mol^{-1}$. Calculate q, w, ΔH, ΔU, ΔS 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. [4] **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**

$$dU = TdS - pdV$$

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

a) $(\partial G/\partial T)_p = -S$ **b)** $(\partial G/\partial p)_T = V$ **c)** $(\partial V/\partial T)_p = -(\partial S/\partial p)_T$

4. [6] Calcium carbonate ($CaCO_3$, 100.1 g mol^{-1}) is found in nature in two different crystalline forms: aragonite (mined in Aragon, a province of Spain) and calcite.

Data at 25 °C and 1 bar:

	aragonite	calcite
$\Delta H_{fm}^{\circ}/(kJ\ mol^{-1})$	−1207.13	−1206.92
$S_m^{\circ}/(J\ K^{-1}\ mol^{-1})$	88.7	92.9
density/(g cm^{-3})	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. [2] 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.)

Chemistry 231 $\boxed{\text{Assignment \#7}}$

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

$$\underset{900\ K}{LiH(s)} \xrightarrow[\text{the solid}]{heat} \underset{961.8K}{LiH(s)} \xrightarrow{melt} \underset{961.8K}{LiH(l)} \xrightarrow[\text{the liquid}]{heat} \underset{1000\ K}{LiH(l)}$$

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

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

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

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

ΔV is small, probably $< 1\ cm^3$ (solid and liquid)

$$w = -\int_{V_i}^{V_f} P_{ext}\,dV = -P\int_{V_i}^{V_f} dV = -P\Delta V$$

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

≈ 0.1 J negligible

$$\boxed{w = 0}$$

$$\boxed{\Delta U = q + \cancel{w}^{\,0} = q = 29067\,J}$$

melting the major source of ΔS

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

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

$$= 4.15 + 23.50 + 2.65$$

$$= \boxed{30.30\ J\,K^{-1}}$$

2. a) reversible path:

$$dS = \frac{dq_{rev}}{T} \qquad\qquad p = P_{ext} \qquad dw = -P_{ext}\,dV$$

$$dq_{rev} = TdS \qquad\qquad dw_{rev} = -pdV$$

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

$$\boxed{dU = TdS - pdV}$$

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

use the "chain" rule
$d(TS) = TdS + SdT$

$$= dU - d(TS)$$

$$= dU - TdS - SdT$$

$$= \cancel{TdS} - pdV - \cancel{TdS} - SdT$$

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

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

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

3. $G(T, p)$

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp \qquad \text{eq. 1}$$

$$\text{compare: } dG = -S\,dT + V\,dp \qquad \text{eq. 2}$$

T and p are <u>independent</u> variables

eq. 1 and eq. 2 provide

a) $\left(\frac{\partial G}{\partial T}\right)_p = -S$ b) $\left(\frac{\partial G}{\partial p}\right)_T = V$

c) $\left[\frac{\partial}{\partial p}\underbrace{\left(\frac{\partial G}{\partial T}\right)_p}_{-S}\right]_T = \left[\frac{\partial}{\partial T}\underbrace{\left(\frac{\partial G}{\partial p}\right)_T}_{V}\right]_p$

from a) and b)

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

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

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

$$\boxed{4.\quad CaCO_3(s,\text{aragonite}) \xrightarrow[1\text{ bar}]{25\,°C} CaCO_3(s,\text{calcite})}$$

$$\Delta H° = \Delta H^°_{fm}(\text{calcite}) - \Delta H^°_{fm}(\text{aragonite})$$
$$= -1206.92 - (-1207.13) = 0.21 \text{ kJ}$$
$$= 210 \text{ J} \quad (\text{small!})$$

$$\Delta S° = S^°_m(\text{calcite}) - S^°_m(\text{aragonite})$$
$$= 92.9 - 88.7 \text{ J K}^{-1}$$
$$= 4.2 \text{ J K}^{-1}$$

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

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

$$\Delta G = \Delta(\overbrace{U + pV}^{H} - TS) = \Delta(H - TS)$$

$$\Delta G_{T,p} = \Delta(H - TS) = \Delta H - T\Delta S$$

fixed

at 1 bar ($p°$):

$\Delta H°$ +210 J (unfavorable for a spont. process)

$\Delta S°$ +4.2 J K^{-1} (favorable!)

$$\Delta G^°_T = \Delta H° - T\Delta S°$$

who wins? $\Delta H°$ or $-T\Delta S°$? The suspense mounts!

Note: No mixing here. Pure aragonite → pure calcite

$$\Delta G^°_{298.15K} = (210 \text{ J}) - (298.15 \text{ K})(4.2 \text{ J K}^{-1})$$

spontaneous reaction

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

more stable

$$\boxed{\Delta G^°_{298.15K} = -1042 \text{ J}}$$ for aragonite → calcite

(4. cont.) use: $\left(\frac{\partial G}{\partial p}\right)_T = V$ and $V = \frac{\text{mass}}{\text{density}}$

b) aragonite $\xrightarrow[1\text{ bar}]{25\ ^\circ C}$ calcite spontaneous

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

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

spontaneous forward reaction at 25 °C, 1 bar

$$\Delta G = G_m(\text{calcite}) - G_m(\text{aragonite})$$ take the pressure derivative

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

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

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

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

aragonite $\underset{p}{\overset{25^\circ C}{\rightleftarrows}}$ calcite in equilibrium when $\Delta G = 0$

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

notice: ΔG increases with pressure, aragonite (denser, smaller volume) eventually is stable

$$\Delta G_p = \Delta G^\circ_{p^\circ} + \int_{p^\circ}^{p} \left(\frac{\partial G}{\partial p}\right)_T dp = \Delta G^\circ_{p^\circ} + \int_{p^\circ}^{p} \Delta V\, dp$$

$$\Delta G_p = \Delta G^\circ_{p^\circ} + \Delta V(p - p^\circ)$$

at equilibrium at P: $\Delta G_p = 0$

$$0 = -1042\,J + (2.78 \times 10^{-6})(p - p^\circ)$$

$$p - p^\circ = 3.75 \times 10^{8}\ Pa = 3750\ bar$$

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

(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) $$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dV = -S\,dT + V\,dp$$

$$d\Delta G = \left(\frac{\partial \Delta G}{\partial T}\right)_p dT + \left(\frac{\partial \Delta G}{\partial p}\right)_T dV = -\Delta S\,dT + \Delta V\,dp$$

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

$\Delta G = 0$ (for equilibrium) at 500 °C (773 K) and pressure p

$$\Delta G_{773K,p} = 0 \qquad \Delta G_{298K,1bar} = -1042 \text{ J}$$

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

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

$$1042\text{ J} = (-4.2\text{ J K}^{-1})(475\text{ K}) + (2.78\times10^{-6}\text{ m}^3)(p - 10^5\text{Pa})$$

$$p - 10^5\text{ Pa} = \frac{3037\text{ J}}{2.78\times10^{-6}\text{ m}^3} = 1.09\times10^9\text{ Pa}$$

$$p = 1.09\times10^9 + 10^5 \text{ Pa}$$

$$p = 1.09\times10^9\text{ Pa} = \boxed{10900\text{ bar}}$$

5. $\left(\frac{\partial S}{\partial V}\right)_T$?

suggests
V, T independent variables
and A(T, V)

$$dA = -SdT - pdV$$

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial A}{\partial T}\right)_V\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial V}\right)_T\right]_V$$

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

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

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V}$$

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

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

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

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \frac{\beta}{\kappa}}$$