1a. nonspont at room T, spont at higher T

$\Delta G = \Delta H - T\Delta S$ ΔS must be ⊕, because then an increase in T makes ΔG more negative.

ΔH must be ⊕, otherwise it would be spontaneous at any temp.

b. Estimate T at which $\Delta G° = 0$ (std. conditions)
   find $\Delta H°$, $\Delta S°$

	$CO_{2(g)}$	+	$H_{2(g)}$	→	$CO_{(g)}$	+	$H_2O_{(g)}$
kJ/mol $\Delta H_f°$	-393.5		0		-110.5		-241.82
J/mol·K $S°$	213.6		130.58		197.9		188.83

$\Delta H°_{rxn} = [-110.5 - 241.82] - [-393.5 + 0] = 41.\overline{1}8 \ kJ/mol$

$S°_{rxn} = [197.9 + 188.83] - (213.6 + 130.58) = 42.\overline{5}5 \ J/mol·K$

$\Delta G° = \Delta H° - T\Delta S°$ if $\Delta G° = 0$, then $\Delta H° - T\Delta S° = 0$ so

$\Delta H° = T\Delta S°$ and $T = \dfrac{\Delta H°}{\Delta S°} = \dfrac{41\overline{1}80 \ J/mol}{42.\overline{5}5 \ J/mol·K} = \boxed{968 \ K}$

$= \boxed{695°C}$

Standard conditions: 1 atm partial pressure of each gas. $P_{CO_2} = P_{H_2} = P_{CO} = P_{H_2O} = 1$ atm each.

c. $\Delta G° = \Delta H° - T\Delta S°$ $500°C = 773 k$

$= 41.\overline{1}8 \ kJ/mol - (773 K)(0.042\overline{5}5 \ kJ/k·mol)$

$= 41.\overline{1}8 \ kJ/mol - 32.8\overline{9} \ kJ/mol = 8.2\overline{9} \ kJ/mol$

$\Delta G°$ is ⊕, so nonspontaneous under std. conditions at 500°C.

Another way to tell: ΔH is ⊕ and ΔS is ⊕ so this rxn will get less spontaneous at lower temps.

$\Delta G° = \Delta H° - T\Delta S°$ $\Delta G°$ less ⊖, more ⊕
      ⊕   ⊕
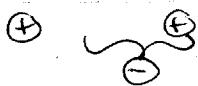
$$Q = \frac{P_{CO}P_{H_2O}}{P_{CO_2}P_{H_2}}$$

1d. $\Delta G = \Delta G° + RT \ln Q$ nonstd. conditions

starts to be spontaneous when $\Delta G = 0$. Use $\Delta G°$ already calculated.

$$0 = 8.29 \times 10^3 \, \text{J/mol} + \left(8.314 \, \text{J/mol·k}\right)\left(773 \, \text{K}\right) \ln Q$$

$$-8.29 \times 10^3 \, \text{J/mol} = 6426.7 \, \text{J/mol} \ln Q$$

$$\frac{}{6426.7} \qquad\qquad \frac{}{6426.7}$$

$$-1.2899 = \ln Q \quad \text{take } e^x \text{ both sides}$$

$$e^{-1.2899} = 0.275 = Q = \frac{(2.0)(P_{H_2O})}{(2.0)(2.0)}$$

$$P_{H_2O} = (0.275)(2.0) = 0.55 = \boxed{0.6 \text{ atm}} \, H_2O$$

2.a. Solubility of AgBr at 40.°C   Need K_{sp} @ 40°C

AgBr$_{(s)}$ $\rightleftharpoons$ Ag$^+$ + Br$^-$ need $\Delta H°$, $\Delta S°$

$\Delta H_f°$ -100.4 105.6 -121.6 KJ/mol

$S°$ 107 72.68 82.4 J/k·mol

$$\Delta H°_{rxn} = [105.6 - 121.6] - [-100.4] = 84.4 \text{ KJ/mol}$$

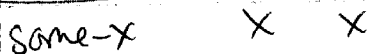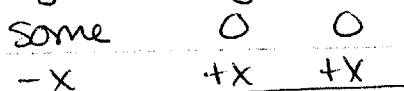$$S°_{rxn} = (72.68 + 82.4) - (107) = 48.08 \text{ J/mol·k}$$

$$\Delta G° = \Delta H° - T\Delta S° = -RT \ln K$$

$$= (84400 \, \text{J/mol}) - (313 \text{ K})(48.08 \, \text{J/mol·k})$$

$$84400 \quad - 15049 \quad = 69351 \quad \text{J/mol}$$

$$\frac{69351 \, \text{J/mol}}{-RT} = \frac{-RT \ln K}{-RT}$$

$$K = e^{-\Delta G°/RT} = e^{\left(\frac{-69351}{8.314)(313)}\right)} = e^{-26.65} \qquad (\text{no sig figs!})$$

$$= 2.7 \times 10^{-12}$$

$$= K_{sp}$$

AgBr $\rightleftharpoons$ Ag$^+$ + Br$^-$

some	0	0
$-x$	$+x$	$+x$
some$-x$	x	x

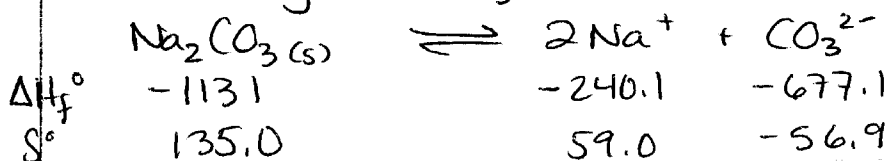solubility

$$K_{sp} = [Ag^+][Br^-] = x^2$$

$$x = \sqrt{K_{sp}} = \sqrt{2.7 \times 10^{-12}} = \boxed{1.63 \times 10^{-6} \, M}$$

$$\left(1.63 \times 10^{-6} \frac{\text{mol}}{L} \text{AgBr}\right)\left(\frac{187.84}{\text{mol}}\right) = \boxed{3 \times 10^{-4} \, g/L}$$

2.b. Solubility of Na_2CO_3 at 75°C - Need K_{sp} @ 75°C

$$Na_2CO_3 {(s)} \rightleftharpoons 2Na^+ + CO_3^{2-}$$

ΔH_f° −1131   −240.1   −677.1

S° 135.0   59.0   −56.9

$\Delta H_{rxn}^\circ = \left[2(-240.1)+(-677.1)\right] - \left[-1131\right] = -26.3 \ kJ/mol$

$S_{rxn}^\circ = \left[2(59.0)+(-56.9)\right] - \left[135.0\right] = -73.9 \ J/mol\cdot K$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT \ln K$

$\quad = -26300 \ J/mol - (348K)(-73.9 \ J/k\cdot mol) =$

$\quad = -26300 + 25717 \quad = -582.8 \ J/mol \qquad$ (no sig figs!)

$\Delta G^\circ = -RT \ln K$

$K = e^{(-\Delta G^\circ / RT)} = e^{\left(\frac{+582.8 \ J/mol}{8.314 \cdot 348}\right)} = e^{(0.20)} = 1.223 = K = K_{sp}$ (no sf)

$$Na_2CO_3 \rightleftharpoons 2Na^+ + CO_3^{2-}$$

Same	0	0
−x	+2x	+x
Same −x	2x	x

$K_{sp} = (2x)^2(x) = 4x^3$

$x = \sqrt[3]{\dfrac{K_{sp}}{4}} = \sqrt[3]{\dfrac{1.223}{4}}$

$x = 0.674 \ M \ Na_2CO_3$

$\left(\dfrac{0.674 \ mol \ Na_2CO_3}{L}\right)\left(\dfrac{105.99g}{1 \ mol}\right) = 71 \ g/L \quad \boxed{approx \ 70 \ g/L}$ (no sf)

3. Normal bp
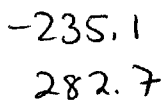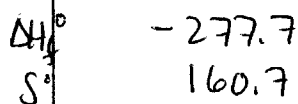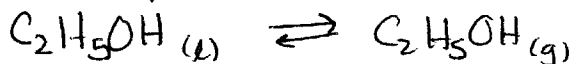
$$C_2H_5OH_{(\ell)} \rightleftharpoons C_2H_5OH_{(g)}$$

$K = \dots P_{C_2H_5OH} = 1.0 \ atm$

so K = 1 at the normal bp

find ΔH_{rxn}°, S_{rxn}°

find T at which K = 1

ΔH_f° −277.7   −235.1

S° 160.7   282.7

$\Delta H^\circ = (-235.1) - (-277.7) = +42.6 \ kJ/mol$

$\Delta S^\circ = (282.7) - (160.7) = +122.0 \ J/k\cdot mol$

(4)

$\Delta G^° = -RT \ln K$ if $K = 1$, $\ln K = 0$, so $\Delta G^° = \emptyset$

$0 = \Delta H^° - T\Delta S^°$

$\Delta H^° = T\Delta S^°$

$T = \dfrac{\Delta H^°}{\Delta S^°} = \dfrac{42600 \text{ J/mol}}{122.0 \text{ J/mol·k}} = 349 \text{ K} = \boxed{76°C}$

b. actual bp of 78°C is very close to 76°C!

4. vp ethanol @ 37°C.   Same rxn: $C_2H_5OH_{(l)} \rightleftharpoons C_2H_5OH_{(g)}$

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

$= 42600 - (310.\text{k})(122.0 \text{J/mol·k}) = 42\bar{6}00 - 37\bar{8}20$

$\Delta G^° = 4\bar{7}80 \text{ J/mol}$

$\Delta G^° = -RT \ln K$ $K = P_{C_2H_5OH}$

$K = e^{\left(\frac{-\Delta G^°}{RT}\right)} = e^{\left(\frac{-4\bar{7}80}{(8.314)(310)}\right)} = e^{-1.8546} = 0.\bar{1}565$

$K = P_{C_2H_5OH} = 0.\bar{1}565 \text{ atm}$

$\left(0.\bar{1}565 \text{ atm}\right)\left(\dfrac{760 \text{ mmHg}}{1 \text{ atm}}\right) = 119 \text{ mmHg}$ $\boxed{vp = \sim 0.2 \text{ atm} \atop \text{or} \sim 100 \text{ mmHg}}$

5. T at which vp = 500. mmHg $C_2H_5OH_{(g)} \rightleftharpoons C_2H_5OH_{(l)}$

$\Delta G^° = \Delta H^° - T\Delta S^° = -RT \ln K$ $K = P_{C_2H_5OH}$

$\Delta H^° = T\Delta S^° - RT \ln K$

$\Delta H^° = T(\Delta S^° - R \ln K)$ $\left(500. \text{ mmHg}\right)\left(\dfrac{1 \text{ atm}}{760 \text{ mmHg}}\right) = 0.6\bar{5}79 \text{ atm}$

$\dfrac{\Delta H^°}{\Delta S^° - R \ln K} = T$

Use $\Delta H^°$, $\Delta S^°$ from prob # 3

$T = \dfrac{42600 \text{ J/mol}}{\left(122.0 \text{ J/mol·k}\right) - \left(8.314 \text{ J/mol·k}\right) \ln(0.6\bar{5}79)}$

$-0.4\bar{1}87$

$3.4\bar{8}115$

$122.0 + 3.4\bar{8}115 = 125.\bar{4}81$

$T = \dfrac{42\bar{6}00 \text{ J/mol}}{125.\bar{4}81 \text{ J/mol·k}} = 339.\bar{4}9 \text{ K} \Rightarrow \boxed{66°C} = \text{bp ethanol at 500 mmHg}$

6. ΔS should be ⊕ —producing more moles gas— entropy increases.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ Raise temp to make it more
                    ⊕   spontaneous. Then ΔG is more

likely to be ⊖.

7. 5.5°C = mp benzene   benzene$_{(s)} \rightleftharpoons$ benzene$_{(\ell)}$

a. melting requires heat. ΔH° is ⊕

b. s → ℓ gets more disordered. ΔS° is ⊕

c. ΔG° at 5.5°C – equilibrium mp. ΔG° = 0

d. ΔG° at 0°C – melting will be nonspontaneous below
   the mp.   ΔG° ⊕

e. ΔG° and 25.0°C – melting will be spontaneous above mp. ΔG° ⊖

8 a. Find ΔG° at each temp. $\Delta G^\circ = -RT\ln K = \Delta H^\circ - T\Delta S^\circ$

$\Delta G^\circ = -(8.314)(303K)\ln(1.66\times10^{-5}) = 27726$ J/mol @ 30.°C
                                        -11.006

$\Delta G^\circ = -(8.314)(373K)\ln(0.231) = 4544$ J/mol @ 100°C
                                -1.465

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

$27726 = \Delta H^\circ - 303K(\Delta S^\circ)$

subtract   ⊖ $4544 = _{\ominus}\Delta H^\circ - _{\oplus}373K(\Delta S^\circ)$
change
signs

$\dfrac{23182}{70} = \dfrac{70\,\Delta S^\circ}{70}$ → $\Delta H^\circ = \Delta G^\circ + T\Delta S^\circ$

$\Delta H^\circ = 27726 + (303)(331)$

$\boxed{\Delta S^\circ = 331 \text{ J/mol·K}}$ $27726 + 100345$

$\Delta H^\circ = 128071$ J/mol

$\boxed{\Delta H^\circ = 128 \text{ kJ/mol}}$