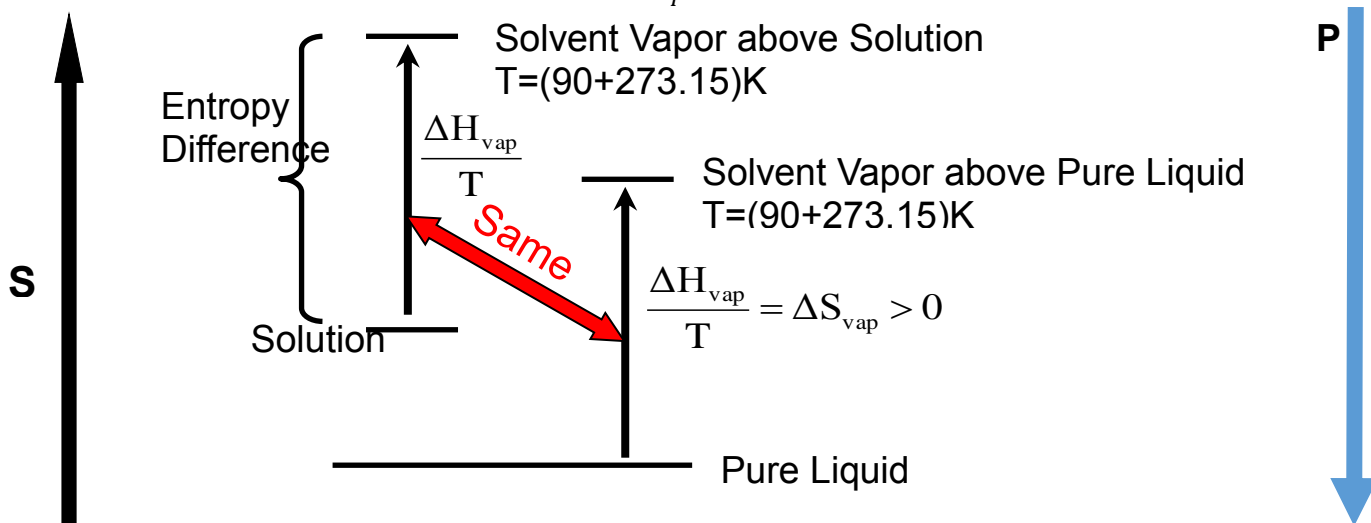


Handout 12 selected solutions:

3. At 90 °C the vapor pressure of water is 0.9 atm and the vapor pressure of an aqueous glucose solution is 0.8 atm. Construct an entropy diagram for vapor pressure lowering and answer the questions below using your drawing. (Hint: have both entropy and pressure scales, and remember that $S \sim W \sim V \sim \frac{1}{P}$)



- ΔH_{vap} (water, $l \rightarrow$ water, g) compared to ΔH_{vap} (glucose solution, $l \rightarrow$ water, g) is...

Greater smaller the same

- S (water, l) compared to S (glucose solution, l) is... Greater smaller
the same

- S (water, g) compared to S (glucose solution, g) is...

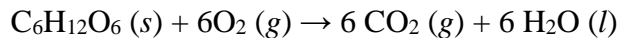
Greater smaller the same

- ΔS_{vap} (water, $l \rightarrow$ water, g) compared to ΔS_{vap} (glucose solution, $l \rightarrow$ water, g) is...

Greater smaller the same

5. For the following combustion reaction calculate ΔG° at 25°C . :

	$\Delta G_f^\circ(\text{kJ/mol})$ (only at 25°C)
$\text{O}_2(\text{g})$	0
$\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	-900.
$\text{CO}_2(\text{g})$	-400.
$\text{H}_2\text{O}(\text{l})$	-240.

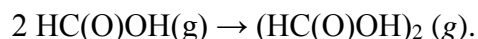


$$\Delta G^\circ = -2940\text{kJ/mol}$$

Without doing a calculation, at what temperatures will this process cease to be spontaneous? NOT EVER

$$\Delta H^\circ_{\text{sys}} < 0 \text{ (exothermic)} \quad \Delta S^\circ_{\text{sys}} > 0$$

12. Here are thermodynamic data for the gas phase dimerization. Calculate equilibrium constant at 37°C for the dimerization.



$$\Delta H_f^\circ(\text{HC}(\text{O})\text{OH}(\text{g})) = -350.0\text{ kJ/mol},$$

$$\Delta H_f^\circ((\text{HC}(\text{O})\text{OH})_2(\text{g})) = -800.0\text{ kJ/mol},$$

$$S^\circ(\text{HC}(\text{O})\text{OH}(\text{g})) = 250.0\text{ J/(K mol)},$$

$$S^\circ((\text{HC}(\text{O})\text{OH})_2(\text{g})) = 350.0\text{ J/(K mol)}.$$

$$\Delta H_{\text{rct}}^\circ = -100.0\text{ kJ/mol}$$

$$\Delta S^\circ = 350.0\text{ J/(K mol)} - 2 \cdot 250.0\text{ J/(K mol)} = -150.0\text{ J/(K mol)};$$

$$\Delta G^\circ = \Delta H_{\text{rct}}^\circ - T \Delta S^\circ = -53.48\text{ kJ/mol} \quad K = 1.0399 \cdot 10^9$$

- a. Calculate the ΔG of dimerization reaction when the pressure of $\text{HC}(\text{O})\text{OH}$ is at 2.0 bars and the pressure of $(\text{HC}(\text{O})\text{OH})_2$ is at 3.5 bars.

$$Q = \frac{[(\text{HC}(\text{O})\text{OH})_2]}{[\text{HC}(\text{O})\text{OH}]^2} = 0.875$$

$$\Delta G = \Delta G^\circ + R \cdot T \cdot 2.303 \log Q = -53.84\text{ kJ/mol}$$

- b. Calculate the total energy available for useful work from the dimerization of 1.00 kg of the reactant used at 37°C .

$$\text{Mole of RXN: } 1000\text{g HC}(\text{O})\text{OH} \cdot \frac{1\text{mol HC}(\text{O})\text{OH}}{46\text{g HC}(\text{O})\text{OH}} \cdot \frac{1\text{mol RXN}}{2\text{mol HC}(\text{O})\text{OH}} = 10.87\text{mol RXN}$$

$$\text{Energy available for useful work} = -53.84 \frac{\text{kJ}}{\text{mol}} \cdot 10.87\text{mol RXN} = -585.2\text{kJ}$$

13. For autoionization of water at 330 K, $K_w=10^{-13}$ and at 300K, $K_w=10^{-14}$. Calculate the value of ΔH and ΔS . Do your calculations to 1 significant figure.

$$\ln K_1 = -\frac{\Delta H_{sys}^{\circ}}{RT_1} + \frac{\Delta S_{sys}^{\circ}}{R} \quad T_1=330 \text{ K, } K_w=10^{-13}$$

—

$$\ln K_2 = -\frac{\Delta H_{sys}^{\circ}}{RT_2} + \frac{\Delta S_{sys}^{\circ}}{R} \quad T_2= 300\text{K, } K_w=10^{-14}$$

$$(\ln K_1 - \ln K_2) = \ln \frac{K_1}{K_2} = -\frac{\Delta H_{sys}^{\circ}}{RT_1} + \frac{\Delta H_{sys}^{\circ}}{RT_2} = \Delta H_{sys}^{\circ} \left(\frac{T_1 - T_2}{RT_2 T_1} \right);$$

$$\Delta H^{\circ} = \frac{\ln \frac{K_1}{K_2} \cdot T_1 \cdot T_2 \cdot R}{T_1 - T_2} = \Delta H = 63174\text{J} = 60\text{kJ}$$

$$\Delta S^{\circ} = \left(\ln K_1 + \frac{\Delta H_{sys}^{\circ}}{RT_1} \right) \cdot R = -57.43 \frac{\text{J}}{\text{molK}} = -60 \frac{\text{J}}{\text{molK}}$$

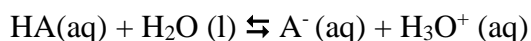
19. Calculate the temperature (in K) at which melting 36.0 grams of water (molar mass of water is 18.0 g/mol) changes the entropy of the universe by -16.0 J/K . For water, $\Delta_{fus}H = 6.00 \text{ kJ/mol}$ and $\Delta_{fus}S = 22.0 \text{ J/(mol K)}$.

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surrounding} = \Delta S_{system} - \frac{\Delta H_{system}}{T_{sur}}$$

Since we have 2 moles of water:

$$-16.0 \text{ J/K} = 22.0 \text{ J/(mol K)} \cdot 2\text{moles} - \frac{6.00 \frac{\text{kJ}}{\text{molK}} \cdot 2\text{moles} \cdot 1000 \frac{\text{J}}{\text{kJ}}}{T_{sur}} \quad \underline{\underline{T=200. \text{ K}}}$$

22. You have a buffer with a pH = 5 at two different temperatures: $T_1 = 300 \text{ K}$ and $T_2 = 330 \text{ K}$



You need to have the following ratios of weak acid and conjugate base to make this happen:

$$\text{at } T_1 \rightarrow [\text{A}^{\ominus}]/[\text{HA}] = 1/2$$

$$\text{at } T_2 \rightarrow [\text{A}^{\ominus}]/[\text{HA}] = 1/4$$

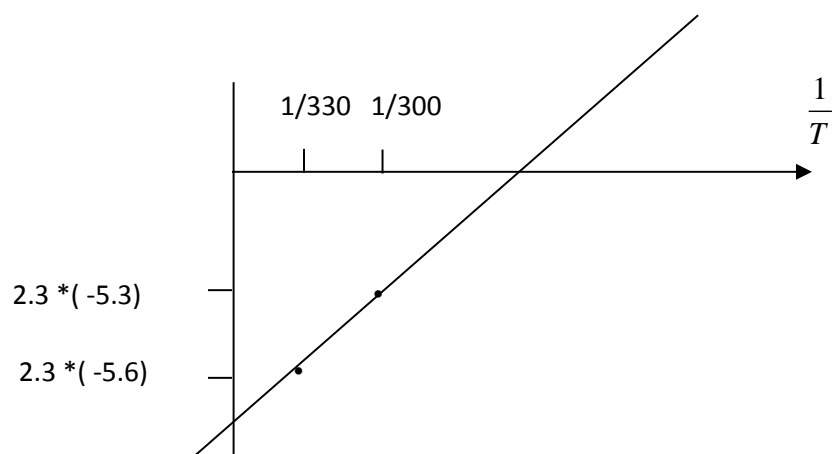
To answer the following questions you need to draw the plot of $\ln K$ verses $1/T$. (Hint: $\ln K = 2.303 \log K$)

$$K_{a1} = \frac{[\text{H}_3\text{O}^{\oplus}][\text{A}^{\ominus}]}{[\text{HA}]} = 10^{-5}/2 \quad K_{a2} = \frac{[\text{H}_3\text{O}^{\oplus}][\text{A}^{\ominus}]}{[\text{HA}]} = 10^{-5}/4$$

$$\log K_{a1} = -5.3 \text{ at } T_1=300\text{K}$$

$$\log K_{a2} = -5.6 \text{ at } T_2=330\text{K}$$

Now that you have $\log K_a$, and $2.3 \log K_a = \ln K_a$, you plot the data...



- a. Will this reaction be exothermic, endothermic or neither. Circle one:
 $\Delta H > 0$ $\Delta H = 0$ $\Delta H < 0$
- b. The system entropy change will be: Circle one:
 $\Delta S > 0$ $\Delta S = 0$ $S < 0$