## Chapter 3 Homework Questions

3.1 Calculate $\Delta S$ (for the system) when the state of 3 . moles of a perfect gas at $25^{\circ} \mathrm{C}$ and 1 . atm is changed to $125{ }^{\circ} \mathrm{C}$ and 5 . atm.
Note: The constant pressure molar heat capacity of this gas is $C_{p, m}=(5 / 2) R$,
3.2 A sample consisting of 3 . moles of a diatomic perfect gas at $-73^{\circ} \mathrm{C}$ is compressed reversibly and adiabically until the temperature reaches $-23 .{ }^{\circ} \mathrm{C}$. For this gas, $\mathrm{C}_{\mathrm{v}, \mathrm{m}}=27.5 \mathrm{~J} / \mathrm{mol} \bullet \mathrm{K}$. Calculate $\mathrm{q}, \mathrm{w}, \Delta \mathrm{U}, \Delta \mathrm{H}$ and $\Delta \mathrm{S}$ for this process.
3.3 Calculate the changes in entropy of the system and the surroundings when a $14 . \mathrm{g}$ sample of $\mathrm{N}_{2}(\mathrm{~g})[\mathrm{M}=28]$ at 1 . bar and $25^{\circ} \mathrm{C}$ doubles its volume in
(a) a reversible isothermal expansion
(b) an irreversible isothermal expansion against $\mathrm{p}_{\mathrm{ex}}=0$.
(c) a reversible adiabatic expansion
3.4 The enthalpy of vaporization of chloroform $\left(\mathrm{CHCl}_{3}, \mathrm{M}=119.4\right)$ is $29.4 \mathrm{~kJ} / \mathrm{mol}$ at its normal boiling point of $62{ }^{\circ} \mathrm{C}$. For the vaporization of 240 . grams of $\mathrm{CHCl}_{3}$ at its normal boiling point, calculate (a) $\Delta \mathrm{S}$ of the system and (b) $\Delta \mathrm{S}$ of the surroundings.
3.5 The normal boiling point of ethanol, $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}[\mathrm{M}=46]$, is $78^{\circ} \mathrm{C}$. The Enthalpy of Vaporization of ethanol is $38.6 \mathrm{~kJ} / \mathrm{mol}$.

Calculate $\mathrm{q}, \mathrm{w}, \Delta \mathrm{U}, \Delta \mathrm{H}$ and $\Delta \mathrm{S}$ when 150 grams of ethanol vapor is condensed to the liquid at $78{ }^{\circ} \mathrm{C}$ and 1 bar pressure.
3.6 The normal melting point of ethanol, $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}[\mathrm{M}=46]$, is $-114{ }^{\circ} \mathrm{C}$. The Enthalpy of Fusion of ethanol is $9.45 \mathrm{~kJ} / \mathrm{mol}$.

Calculate $\mathrm{q}, \mathrm{w}, \Delta \mathrm{U}, \Delta \mathrm{H}$ and $\Delta \mathrm{S}$ when 150 grams of ethanol liquid crystallizes to the solid at $-114{ }^{\circ} \mathrm{C}$ and 1 bar pressure.
3.7 The normal boiling point of benzene is $80^{\circ} \mathrm{C}=353 \mathrm{~K}$. The enthalpy of vaporization of benzene at its normal boiling point is $\Delta_{\text {vap }} \mathrm{H}=35.7 \mathrm{~kJ} / \mathrm{mol}$. The constant pressure molar heat capacities of the liquid and vapor are: $\mathrm{C}_{\mathrm{p}, \mathrm{m}}(\mathrm{l})=138.7 \mathrm{~J} / \mathrm{mol}-\mathrm{K}$ and $\mathrm{C}_{\mathrm{p}, \mathrm{m}}(\mathrm{g})=35.1 \mathrm{~J} / \mathrm{mol}-\mathrm{K}$

Consider the vaporization of one mole of superheated benzene at 100 oC . Calculate $\Delta$ Ssys, $\Delta S_{\text {surr, }}$, and $\Delta S_{\text {univ }}$ for this process.
3.8 The standard molar entropy of $\mathrm{NH}_{3}(\mathrm{~g})$ is $192.45 \mathrm{~J} / \mathrm{mol} \bullet \mathrm{K}$ at $25^{\circ} \mathrm{C}$. The constant pressure heat capacity is temperature dependent and is given by:
$C_{p, m}=a+b T+\frac{c}{T^{2}} \quad \mathrm{a}=29.8 \quad, \mathrm{~b}=2.5 \times 10^{-2}, \quad \mathrm{c}=-1.6 \times 10^{5}$
Calculate the entropy of 3 . moles of $\mathrm{NH}_{3}(\mathrm{~g})$ at:
(a) $100{ }^{\circ} \mathrm{C}$
(b) $500{ }^{\circ} \mathrm{C}$
3.9 The constant pressure heat capacity of $\mathrm{F}_{2}(\mathrm{~g})$ is temperature dependent and given by:

$$
C_{p, m}=a-\frac{b}{T} \quad \mathrm{a}=39.6 \mathrm{~J} / \mathrm{mol}-\mathrm{K} \text { and } \mathrm{b}=2.5 \times 10^{3} \mathrm{~J} / \mathrm{mol}
$$

Consider 100 grams of $\mathrm{F}_{2}(\mathrm{~g})$ [ $\mathrm{M}=38$.] initially at a pressure of 2 . bar and temperature of $600^{\circ} \mathrm{C}$. Calculate $\mathrm{q}, \mathrm{w}, \Delta \mathrm{U}, \Delta \mathrm{H}, \Delta \mathrm{S}$ for each of the following processes.
(a) The gas is cooled to $300^{\circ} \mathrm{C}$ at constant pressure.
(b) The gas is cooled to $300^{\circ} \mathrm{C}$ at constant volume
3.10 Use the standard molar entropies (at 298 K ) in the table below to calculate the reaction entropies, $\Delta_{\mathrm{r}} \mathrm{S}^{0}$, for the following reactions.
(a) $2 \mathrm{CH}_{3} \mathrm{CHO}(\mathrm{g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{l})$
(b) $\mathrm{Hg}(\mathrm{l})+\mathrm{Cl}_{2}(\mathrm{~g}) \rightarrow \mathrm{HgCl}_{2}(\mathrm{~s})$.

## Compound $\mathbf{S}_{\mathbf{m}}{ }^{\mathbf{0}}$

$\mathrm{CH}_{3} \mathrm{CHO}(\mathrm{g}) \quad 250.3 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K}$
$\mathrm{O}_{2}(\mathrm{~g}) \quad 205.1$
$\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{l}) \quad 159.8$
$\mathrm{Hg}(\mathrm{l}) \quad 76.0$
$\mathrm{Cl}_{2}(\mathrm{~g}) \quad 223.1$
$\mathrm{HgCl}_{2}(\mathrm{~s}) \quad 146.0$
3.11 Use the standard Gibbs Energies of Formation (at 298 K ) in the table below to calculate the reaction entropies, $\Delta_{\mathrm{r}} \mathrm{S}^{0}$, for the following reactions.
(a) $2 \mathrm{CH}_{3} \mathrm{CHO}(\mathrm{g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{l})$
(b) $\mathrm{Hg}(\mathrm{l})+\mathrm{Cl}_{2}(\mathrm{~g}) \rightarrow \mathrm{HgCl}_{2}(\mathrm{~s})$.

## Compound $\Delta_{f} \mathbf{G}_{\mathbf{m}}{ }^{\mathbf{0}}$

$\mathrm{CH}_{3} \mathrm{CHO}(\mathrm{g}) \quad-128.9 \mathrm{~kJ} / \mathrm{mol}$
$\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{l}) \quad-389.9$
$\mathrm{HgCl}_{2}(\mathrm{~s}) \quad-178.6$
3.12 Use the standard molar entropies and the enthalpies of formation in the table below to calculate the standard Gibbs energy change (at 298 K ) for the reaction:
$4 \mathrm{HCl}(\mathrm{g})+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{Cl}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$

| Compound | $\mathbf{S}_{\mathbf{m}}^{\mathbf{0}}$ | $\Delta_{\mathbf{f}} \mathbf{H}_{\mathbf{m}}{ }^{\mathbf{0}}$ |
| :--- | :---: | :--- |
| $\mathrm{HCl}(\mathrm{g})$ | $186.9 \mathrm{~J} / \mathrm{mol} \cdot \mathrm{K}$ | $-92.3 \mathrm{~kJ} / \mathrm{mol}$ |
| $\mathrm{O}_{2}(\mathrm{~g})$ | 205.1 |  |
| $\mathrm{Cl}_{2}(\mathrm{~g})$ | 69.9 |  |
| $\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ | 223.1 | -285.8 |

3.13 Consider 70. grams of $\mathrm{N}_{2}(\mathrm{~g})[\mathrm{M}=28]$ initially at $40^{\circ} \mathrm{C}$ and 25 L . The gas is compressed isothermally to a final volume of 500 mL . Calculate $\Delta \mathrm{G}$ for this process.
3.14 The change in the Gibbs Energy for a certain constant pressure process is given by: $\Delta \mathrm{G}=\mathrm{a}+\mathrm{bT}^{2}, \mathrm{a}=+5620 \mathrm{~J}, \mathrm{~b}=8.0 \times 10^{-2} \mathrm{~J} / \mathrm{K}^{2}$.
Calculate $\Delta \mathrm{S}$ for this process at $30^{\circ} \mathrm{C}$ (in $\mathrm{J} / \mathrm{K}$ )
3.15 Calculate the change in Gibbs Energy (in J) of 20. moles of liquid benzene $\left(\mathrm{C}_{6} \mathrm{H}_{6}, \mathrm{M}=78 \mathrm{~g} / \mathrm{mol}, \mathrm{d}=0.88 \mathrm{~g} / \mathrm{mL}\right)$ when the pressure on the sample is increased from 1.0 atm to 100 atm .
3.16 Calculate the change in Gibbs Energy (in J) of 20. moles of $\mathrm{H}_{2}(\mathrm{~g})$ when the pressure on the sample is increased from 1.0 atm to 100 atm at $25^{\circ} \mathrm{C}$.
3.17 A solid has two crystalline forms, $A(s)$ and $B(s)$. For the transition $A(s) \rightarrow B(s), \Delta G^{0}=+6.0$ $\mathrm{kJ} / \mathrm{mol}$ (i.e. at 1 bar pressure). The difference in molar volumes of the two forms is $\mathrm{Vm}(\mathrm{B})-\mathrm{Vm}(\mathrm{A})=\Delta \mathrm{Vm}=-15 \mathrm{~mL} / \mathrm{mol}$.
Calculate the pressure, in bar, at which the two forms will be in equilibrium.

