Pg 1

HWK #4 Ans key

21-4 $\bar{C}_V(T)/R = 16.4105 - \frac{6085.929\,K}{T} + \frac{822826\,K^2}{T^2}$ 300-1000K

$$\Delta S = \int_{T_1}^{T_2} \frac{n\bar{C}_V}{T}\,dT \qquad n = 1 \text{ mol}$$

$$\int_{T_1}^{T_2} \frac{\bar{C}_V}{T} dT = \int_{300}^{\overset{600}{\cancel{1000}}} \frac{16.4105}{T} - \frac{6085.929}{T^2} + \frac{822826}{T^3}\,dT$$

$$= 16.4105 \ln T - \frac{6085.929\cancel{(-2)}}{-T} + \frac{822826}{(-2)T^2}\Bigg|_{300}^{\overset{600}{\cancel{1000}}}$$

$$= 16.4105 \ln(\overset{600}{\cancel{1000}}) - 16.4105 \ln(300) + \frac{6085.929}{\underset{600}{\cancel{1000}}} - \frac{6085.929}{300}$$
$$- \frac{411413}{\underset{600}{\cancel{1000}}^2} + \frac{411413}{300^2}$$

$$= \cancel{9.72}\ 4.66$$

$$\Delta S = (4.66R)(1 \text{ mol}) = 38.75 \text{ J/K}$$

21-5 we need $\bar{C}_P$. For an ideal gas $\bar{C}_P = R + \bar{C}_V$

$$\text{so } \bar{C}_P/R = 1 + 16.4105 - \frac{6085.929\,K}{T} + \frac{822826\,K^2}{T^2}$$

$$\int_{T_1}^{T_2} \frac{\bar{C}_V}{T} dT = \int_{300}^{600} \frac{17.4105}{T} - \frac{6085.929}{T^2} + \frac{822826}{T^3}\,dT$$

$$= 17.4105 \ln T - \frac{6085.929}{-T} + \frac{822826}{(-2)T^2}\Bigg|_{300}^{600}$$

$$= 5.353$$

$$\Delta S = (5.353R)(1 \text{ mol}) = 44.51 \text{ J/K}$$

Pg 2

21-12 why is $\Delta_{vap}\bar{S} > \Delta_{fus}\bar{S}$?

- $\Delta_{vap}\bar{S}$ is a transition from liquid to gas. Gases are <u>much</u> more disordered than liquids.
- $\Delta_{fus}\bar{S}$ is a transition from solid to liquid. Liquids are <u>somewhat</u> more disordered than solids.

21-14

$$\begin{aligned}\bar{S}(T) = {} & \overset{\text{Debye approx}}{\downarrow}\frac{\bar{C}_p(10K)}{3} + \int_{10}^{35.61} \frac{\bar{C}_p[N_2(s_1)]}{T}\,dT + \frac{\Delta_{trs}\bar{H}}{35.61} \\ & + \int_{35.61}^{63.51} \frac{\bar{C}_p[N_2(s_2)]}{T}\,dT + \frac{\Delta_{fus}\bar{H}}{63.51} \\ & + \int_{63.51}^{77.36} \frac{\bar{C}_p[N_2(l)]}{T}\,dT + \frac{\Delta_{vap}\bar{H}}{77.36} \\ & + \int_{77.36}^{298.15} \frac{\bar{C}_p[N_2(g)]}{T}\,dT + \text{correction}\end{aligned}$$

↑

Do integrals in mathcad (see attached)

$$\begin{aligned} & = \frac{6.15}{3} + 25.86 + \frac{228.9}{35.61} + 23.41 + \frac{710}{63.51} \\ & \quad + 11.78 + \frac{5570}{77.36} + 39.26 + 0.02 \end{aligned}$$

$$= 192.05 \text{ J/K}\cdot\text{mol}$$

21-40 a CO_2 (more atoms)

b $CH_3CH_2CH_3$ (more flexibility / vibrations)

c $CH_3CH_2CH_2CH_2CH_3$ (")

21-43 $c > b \approx d > a$

$\Delta n_g = -1$ $\Delta n_g = -2$ $\Delta n_g = -3$

2.

$$Q = \left(\frac{2\pi M k_B T}{h^2}\right)^{3N/2} \frac{V^N}{N!} \left(\frac{T}{\sigma \Theta_{rot}}\right)^N \left(\frac{e^{-\Theta_{vib}/2T}}{1-e^{-\Theta_{vib}/T}}\right)^N g_{e1}^N \, e^{ND_e/k_BT}$$

a)

$$S = k_B \ln Q + k_B T \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

$$\ln Q = \frac{3N}{2} \ln\left(\frac{2\pi M k_B}{h^2}\right) + \frac{3N}{2} \ln T + N \ln V - \overset{\substack{N\ln N - N \\ \downarrow}}{\ln N!} + N \ln\left(\frac{T}{\sigma \Theta_{rot}}\right)$$

$$+ N \ln e^{-\Theta_{vib}/2T} - N \ln(1-e^{-\Theta_{vib}/T}) + N \ln g_{e1} + \cancel{\ln e}^{ND_e/k_BT}$$

$$= N\left[\frac{3}{2} \ln\left(\frac{2\pi M k_B}{h^2}\right) + \frac{3}{2}\ln T + \ln V - \ln N + 1 + \overset{+\ln T - \ln(\sigma\Theta_{rot})}{\ln\left(\frac{T}{\sigma\Theta_{rot}}\right)} - \frac{\Theta_{vib}}{2T} - \ln(1-e^{-\Theta_{vib}/T}) + \ln g_{e1} + D_e/k_BT\right]$$

$$\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = \frac{3N}{2}\cdot\frac{1}{T} + \frac{N}{T} + \frac{N\Theta_{vib}}{2T^2} - \frac{N}{1-e^{-\Theta_{vib}/T}}\cdot\frac{\Theta_{vib}}{T^2} - \frac{ND_e}{k_BT^2}$$

$R = \frac{k_BN}{n}$

$$k_BT\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = \frac{3k_BN}{2} + k_BN + \frac{k_BN\Theta_{vib}}{2T} - \frac{\overset{k_BN}{\Theta_{vib}/T}}{1-e^{-\Theta_{vib}/T}} - \frac{ND_e}{T}$$

$$= Nk_B\left(\frac{5}{2} + \frac{\Theta_{vib}}{2T} - \frac{\Theta_{vib}/T}{1-e^{-\Theta_{vib}/T}} - \frac{D_e}{T}\right)$$

$$k_B \ln Q = Nk_B\left[\frac{3}{2}\ln\left(\frac{2\pi M k_B T}{h^2}\right) + \ln V - \ln N + 1 + \ln\frac{T}{\sigma\Theta_{rot}} + \ln e^{-\Theta_{vib}/2T} + \ln g_{e1} - \ln(1-e^{-\Theta_{vib}/T}) + \frac{D_e}{k_BT}\right]$$

$$\frac{\bar{S}}{R} = \ln\left[\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2}\cdot\frac{V}{N}\right] + \ln\left(\frac{Te}{\sigma\Theta_{rot}}\right) - \cancel{\frac{\Theta_{vib}}{2T}} - \ln(1-e^{-\Theta_{vib}/T}) + \ln g_{e1} + \cancel{\frac{D_e}{k_BT}}$$

$$+ \frac{5}{2} + \cancel{\frac{\Theta_{vib}}{2T}} - \frac{\Theta_{vib}/T}{1-e^{-\Theta_{vib}/T}} - \cancel{\frac{D_e}{T}}$$

$$\therefore \frac{\bar{S}}{R} = \ln\left[\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2}\frac{V e^{5/2}}{N}\right] + \ln\left(\frac{Te}{\sigma\Theta_{rot}}\right) - \ln(1-e^{-\Theta_{vib}/T}) - \frac{\Theta_{vib}/T}{1-e^{-\Theta_{vib}/T}} + \ln g$$

$$\text{Eq } 21.28: \frac{\bar{S}}{R} = \ln\left[\left(\frac{2\pi M k_B T}{h^2}\right)^{3/2}\frac{\bar{V}}{N_A}e^{5/2}\right] + \ln\left(\frac{Te}{2\Theta_{rot}}\right) - \ln(1-e^{-\Theta_{vib}/T}) + \frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T}-1} + \ln g_{e1}$$

Differences ① ② ③

① $\frac{V}{N} = \frac{\bar{V}n}{N} = \bar{V}/N_A$ ② Book gives Eq 21.28 for N_2 where $\sigma = 2$

③ $\frac{-\Theta_{vib}/T}{1-e^{-\Theta_{vib}/T}} = \frac{+\Theta_{vib}/T}{e^{-\Theta_{vib}/T}-1}$

b) CO $\Theta_{rot} = 2.77\ K$ $T = 81.6\ K$ $P = 1\ bar$

$\Theta_{vib} = 3103\ K$ $\sigma = 1$, $g_{e1} = 1$ ↖ (normal b.p.)

$$\frac{2\pi M k_B T}{h^2} = \left[\frac{2\pi(4.65\times10^{-26}\,kg)(1.3807\times10^{-23}\,J/K)(81.6\,K)}{(6.626\times10^{-34}\,J\cdot s)^2}\right]^{3/2}$$

$$= 2.05\times10^{31}\ m^{-3}$$

$$\frac{\overline{V}}{N_A} = \frac{RT}{N_A P} = \frac{(0.08314\ L\cdot bar/mol\cdot K)(81.6\ K)}{(6.022\times10^{23}\ mol^{-1})(1\ bar)} = 1.127\times10^{-23}\ L$$

$$= 1.127\times10^{-26}\ m^{3}$$

$$\frac{Te}{\sigma\Theta_{rot}} = \frac{(81.6\,K)(2.71828)}{(1)(2.77\,K)} = 80.076$$

$\ln g_{e1} = 0$

$$1 - e^{-\Theta_{vib}/T} = 1 - e^{-3103/81.6} \approx 1$$

$$\frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T}-1} = \frac{3103/81.6}{e^{3103/81.6}-1} = 1.162\times10^{-15}$$

$$\frac{\overline{S}}{R} = 14.85 + 4.38 - 0 + 1.162\times10^{-15} + 0$$

$$\overline{S} = 159.9\ J/K\cdot mol$$

c) Due to residual entropy, this value differs from experimental value by ~ 5 J/K·mol. (Recall: residual entropy is caused by compounds not crystallizing perfectly.)

Ch 22

1. At 80.09 °C $\underset{\text{@ eq.}}{\Delta G_{vap} = 0}$ T = 353.24 K

$$\Delta G = \Delta H - T\Delta S = 0$$

$$30.72 - 353.24\,\Delta S = 0$$

$$\Delta S = 0.08697 \text{ kJ/k·mol}$$

$$\Delta S_{vap} = 86.97 \text{ J/k·mol}$$

75 °C … 348.15 K

$$\Delta G = 30.72 - 348.15\,(0.08697)$$

$$= 0.4414 \text{ kJ/mol} = 441.4 \text{ J/mol}$$ ← won't spontaneously vaporize

85 °C … 358.15 K

$$\Delta G = 30.72 - 358.15\,(0.08697)$$

$$= -0.4283 \text{ kJ/mol} = -428.3 \text{ J/mol}$$ ← will spontaneously vaporize (boil)

2. $$U - U^{id} = \int \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV'$$ (from Eq 22.22)

$$P = \frac{RT}{\bar V - b} - \frac{a}{\bar V^2} \qquad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{\bar V - b}$$

$$U - U^{id} = \int \left[\cancel{T\left(\frac{R}{\bar V - b}\right)} - \left(\cancel{\frac{RT}{\bar V - b}} - \frac{a}{\bar V^2}\right)\right] dV' \qquad +a\int \frac{1}{\bar V^2}\,dV = +\frac{a}{-\bar V^{-1}}$$

$$= -\frac{a}{\bar V}$$

$$U = U^{id} - a/\bar V$$ ← Watch your units… change $a/\bar V$ to kJ/mol

$a_{ethane} = 5.5818$ dm^6·bar/mol^2 ~~→ 0.05818 J/mol~~

$b_{ethane} = 0.065144$ dm^3/mol

$U^{id} = 14.55$ kJ/mol

$R = 0.08\overset{3145}{\cancel{2058}}$ L·bar/k mol

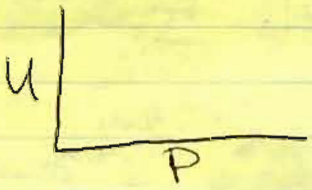
$$P = \frac{RT}{\bar V - b} - \frac{a}{\bar V^2}$$

$\bar V = \frac{dm^3}{mol}$

See attached plot of U vs P

$\bar V$ U P

dm^3 bar = 100 J



3. $\bar{C}_p - \bar{C}_v = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial \bar{V}}{\partial T}\right)_P$

a) $P(\bar{V}-b) = RT$ $\qquad P = \frac{RT}{\bar{V}-b}$ $\qquad \bar{V} = \frac{RT}{P} + b$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{\bar{V}-b}$$

$$\left(\frac{\partial \bar{V}}{\partial T}\right)_P = \frac{R}{P}$$

$$\bar{C}_p - \bar{C}_v = T\left(\frac{R}{\bar{V}-b}\right)\left(\frac{R}{P}\right) = \overset{P}{\frac{RT}{\bar{V}-b}} \cdot \frac{R}{P} = P \cdot \frac{R}{P} = R$$

b) $P\bar{V} = RT$ $\qquad P = \frac{RT}{\bar{V}}$ $\qquad \bar{V} = \frac{RT}{P}$

$$(\partial P/\partial T)_V = R/\bar{V}$$

$$\left(\frac{\partial \bar{V}}{\partial T}\right)_P = R/P$$

$$\bar{C}_p - \bar{C}_v = T(R/\bar{V})(R/P) = P \cdot R/P = R$$

4. $dS = PdV + \frac{1}{T}dU$

The natural variables for entropy are V + U. ~~These~~ Using V + U for the formal/total derivative will yield simple thermodynamic relationships.

5. Natural variables for U are S + V...

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

$$\left(\frac{\partial U}{\partial S \partial V}\right)_S = \left(\frac{\partial T}{\partial V}\right)_S \qquad \left(\frac{\partial U}{\partial V \partial S}\right)_V = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V}$$

6. ΔH_c (glucose) = -2808 kJ/mol $\qquad$ $T = 37 + 273 = 310$ K

$$\Delta G = \Delta H_c - T\Delta S$$
$$= -2808 \text{ kJ/mol} - 310\cancel{K}(0.1824 \text{ kJ/K·mol})$$
$$= -2865 \text{ kJ/mol}$$

For 1 mol... $\quad -2865$ kJ

$\Delta G = w_{non\,PV}$ $\quad$ so we can do maximum of 2865 kJ of work if we consume 1 mol glucose (likely much less in relatity)

7.

	$2\,CO$	+ O_2	$\rightarrow 2CO_2$	
ΔH_f° (kJ/mol)	-110.53	0	-393.51	NIST
ΔS° (J/mol·K)	197.66	205.07	213.79	

@ 298K

$$\Delta H_r = 2(-393.51) - 0 - 2(-110.53) = -565.96 \text{ kJ/mol}$$
$$\Delta S_r = 2(213.79) - 205.07 - 2(197.66) = -172.81 \text{ J/mol·K}$$
$$\Delta G_r = (-565.96) - 298\left(\frac{-172.81}{1000}\right)$$
$$= -514.46 \text{ kJ/mol}$$

From Gibbs-Helmholtz Eq $\quad \dfrac{\Delta_r G(375\,K)}{375} - \dfrac{\Delta_r G(298\,K)}{298} \approx \Delta H(298K)\left(\dfrac{1}{375} - \dfrac{1}{298}\right)$

$$\frac{\Delta_r G(375)}{375} \approx -1.3355$$

$$\Delta_r G(375) \approx -501 \text{ kJ/mol}$$

8. 2 mol gas Initially: 330 K, 3.50 atm

compressed isothermally: 330 K, ↑ P, ↓ V

Entropy drops 25.0 J/k...

$$\boxed{\Delta S = nR \ln\left(V_f/V_i\right)}$$
$$= nR \ln\left(P_i/P_f\right)$$

← since its an ideal gas + constant n + T...

$P_f V_f = P_i V_i$

$V_f/V_i = P_i/P_f$

$$\Delta S/nR = \ln P_i/P_f = -\ln\left(P_f/P_i\right)$$
$$e^{-\Delta S/nR} = P_f/P_i$$
$$P_f = P_i\, e^{-\Delta S/nR}$$
$$= (3.50\text{ atm})\, e^{-25/2\times 8.314}$$
$$\boxed{= 15.7\text{ atm}}$$

$$\Delta G = \overset{0\ (\text{constant } T)}{\cancel{\Delta H}} - T\Delta S$$
$$= -(330\text{K})(-25.0\text{ J/k})$$
$$\boxed{\Delta G = 8.25\text{ kJ}}$$

9. a $\Delta H + \Delta U$ isothermal, reversible... $dT = 0$ $\boxed{\begin{matrix} dU = C_v dT = 0 \\ dH = C_p dT = 0 \end{matrix}}$ $dS = dq/T \neq 0$

$dG = dH - TdS \neq 0$

$dA = dU - TdS \neq 0$

b ΔS adiabatic... $q = 0$ so $\Delta S = 0$

c none

d ΔG ← (equilibrium)

e ΔU

$\Delta H, \Delta G, \Delta S, \Delta U, \Delta A$

$\Delta H = \Delta U + \Delta(PV)$

$+ P\Delta V + V\Delta P$