Lecture 11

Thursday, October 19, 2023 11:31

Midterm Solutions

Originally out of 100

$\boxed{\text{Actually out of 90}}$

Carnot cycle was difficult for many

Question 1: if used incorrect solution, still got full marks (explained below).

① $\Delta_{com}H^{\ominus}(\text{benzene}) = -3268 \text{ kJ}\cdot\text{mol}^{-1}$

$\Delta_{com}H^{\ominus}(\text{cyclohexane}) = -3920 \text{ kJ}\cdot\text{mol}^{-1}$

$$C_6H_6(l) + 3H_2(g) \rightarrow C_6H_{12}(l) \quad (i)$$

$\Delta_r H^{\ominus}(i) = ?$

$$\boxed{\Delta_r H^{\ominus}(i) = \Delta_f H^{\ominus}(C_6H_{12}) - \Delta_f H^{\ominus}(C_6H_6)}$$

many treated $\Delta_{com}H^{\ominus}$ as $\Delta_f H^{\ominus}$.

Write out combustion reactions:

$$C_6H_6(l) + \frac{15}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$$

$$C_6H_{12}(l) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$$

$$\Delta_{com}H^\ominus(C_6H_6) = 6\Delta_f H^\ominus(CO_2) + 3\Delta_f H^\ominus(H_2O)$$

$$- \boxed{\Delta_f H^\ominus(C_6H_6)}$$

$$\boxed{\begin{aligned} \Delta_f H^\ominus(C_6H_6) &= \cancel{6\Delta_f H^\ominus(CO_2)} + \cancel{3\Delta_f H^\ominus(H_2O)} \\ &\quad - \Delta_{com} H^\circ(C_6H_6) \end{aligned}}$$

$$\Delta_{com}H^\ominus(C_6H_{12}) = 6\Delta_f H^\ominus(CO_2) + 6\Delta_f H^\ominus(H_2O)$$

$$- \boxed{\Delta_f H^\ominus(C_6H_{12})}$$

$$\boxed{\begin{aligned} \Delta_f H^\ominus(C_6H_{12}) &= \cancel{6\Delta_f H^\ominus(CO_2)} + \overset{3}{\cancel{6}}\Delta_f H^\ominus(H_2O) \\ &\quad - \Delta_{com} H^\ominus(C_6H_{12}) \end{aligned}}$$

$$\Delta_r H^\ominus(i) = -\Delta_{com}H^\ominus(C_6H_{12}) + \Delta_{com}H^\ominus(C_6H_6)$$

$$+ 3\Delta_f H^\ominus(H_2O)$$

$$= +3920 + (-3268)$$

$$+\ 3\cdot(-268)$$

$$\Delta_r H^\ominus(i) = -206\ \text{kJ}\cdot\text{mol}^{-1}$$

$$\boxed{\Delta_{com} H^\ominus(C_6H_{12}) - \Delta_{com} H^\ominus(C_6H_6)}$$

accepted on the exam

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② Isothermal, reversible expansion

$\Delta U = 0$

$q = q_{rev}$

$w = w_{rev}$

$đw = -p\,dV$

$$w_{rev} = -nRT \ln\frac{V_f}{V_i}$$

$$\Delta U = q + w = q_{rev} + w_{rev}$$

$$q_{rev} = -w_{rev}$$

$$q_{rev} = +nRT \ln\frac{V_f}{V_i}$$

$$n = \frac{m}{M} = \frac{2.9\,g}{39.948\,g\cdot mol^{-1}} = 0.07259\ mol$$

$T = 298\ K$

$$q_{rev} = (0.07259\ mol)(8.3145\ J\cdot mol^{-1}\cdot K^{-1})(298\ K)\ln\left(\frac{4.60\ dm^3}{1.20\ dm^3}\right)$$

$q_{rev} = 241\ J$

$$\Delta S = \frac{q_{rev}}{T}$$

$$= \frac{241\ J}{298\ K}$$

$$\boxed{\Delta S = 0.81\ J\cdot K^{-1}}$$

reversible: $\boxed{\Delta S_{tot} = 0}$

$$\Delta S_{tot} = \Delta S + \Delta S_{sur}$$

$$\Delta S_{sur} = -\Delta S$$

$$\boxed{\Delta S_{sur} = -0.81\ J\cdot K^{-1}}$$

3. $p = \frac{nRT}{V} - \frac{n^2 a}{V^2}$ EOS

$$\boxed{\begin{gathered} pV = nRT \\ p = \frac{nRT}{V} \end{gathered}}$$

a) $w_{rev} = ?$

$$dw_{rev} = -p\,dV$$

$$dw_{rev} = \left(-\frac{nRT}{V} + \frac{n^2 a}{V^2}\right) dV$$

$$w_{rev} = \int_{V_i}^{V_f} \left(-\frac{nRT}{V} + \frac{n^2 a}{V^2}\right) dV$$

$$= -nRT \ln V - \frac{n^2 a}{V} \Bigg|_{V_i}^{V_f}$$

$$\boxed{w_{rev} = -nRT \ln \frac{V_f}{V_i} - n^2 a \left(\frac{1}{V_f} - \frac{1}{V_i}\right)}$$

b) $w_{sur} = \underbrace{+ nRT \ln \frac{V_f}{V_i}}_{\text{perfect gas}} + n^2 a \left(\frac{1}{V_f} - \frac{1}{V_i}\right)$

$V_f > V_i$

$\frac{1}{V_f} - \frac{1}{V_i} < 0$

$\therefore$ Less work is done compared to a perfect gas.

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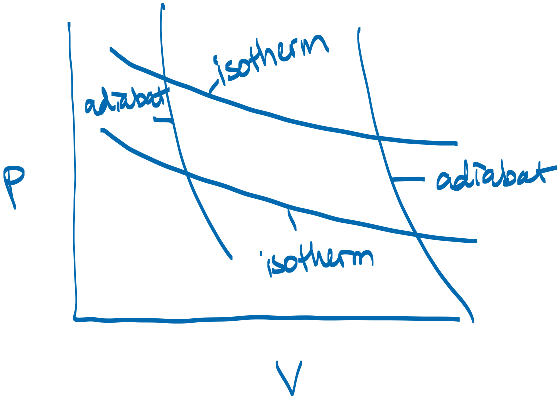
4. a)



b) ΔS overall, ΔS of each stage

ΔS overall $= 0$

ΔS_2, $\Delta S_4 = 0$

Stage 1 :

Isothermal process : $\Delta U = 0$

$$-dw_{rev} = dq_{rev}$$

$$w_{rev} = -nRT \ln\left(\frac{V_f}{V_i}\right)$$

$$q_h = nRT_h \ln\left(\frac{V_B}{V_A}\right)$$

$$\Delta S_1 = \frac{q_h}{T} = nR \ln\left(\frac{V_B}{V_A}\right)$$

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5. "Your hand becoming warmer when it touches ice."

"A ball absorbing thermal energy from the ground and bounces higher."

"The universe begins compressing instead of expanding."

"A machine converts 100% of heat into work."

" A group of high temperature molecules organizing themselves into ordered motion."

great answers!

6. a) $A = U - TS$

$$H = U + pV$$

$$dH = dU + pdV + Vdp$$

$$dA = ?$$

$$\boxed{dA = dU - TdS - SdT}$$

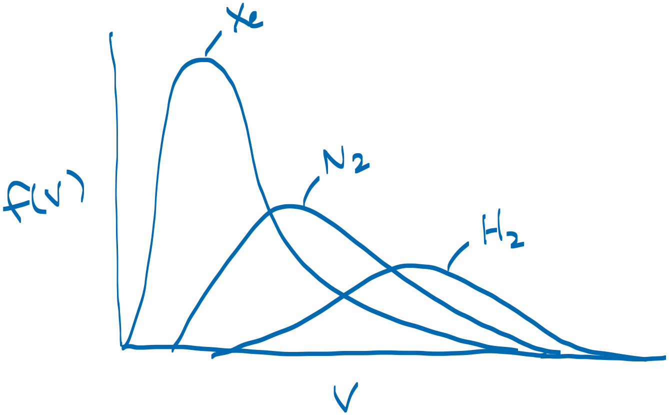
b) $dU = TdS - pdV$

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

$$\boxed{dA = -pdV - SdT}$$

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

7.

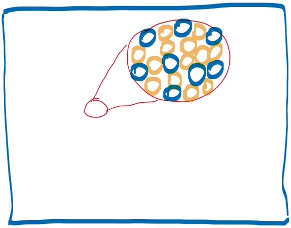


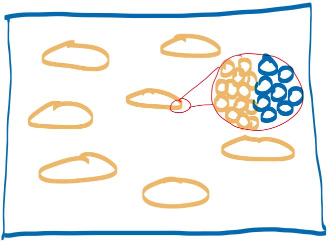
Focus 4: Physical Transformations of Pure Substances

phase: a form of matter that is uniform throughout in chemical composition and physical state

↑

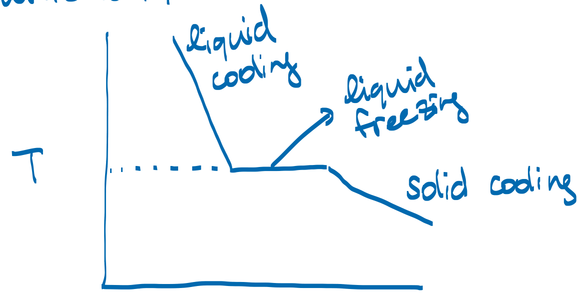
solid, liquid, vapour, allotropes, polymorphs denoted with P


single-phase solution


dispersion with two components

- phase transition: spontaneous conversion of one phase into another phase; for a given pressure, occurs at a characteristic transition temperature, T_{trs}.

At T_{trs}: two phases are in equilibrium

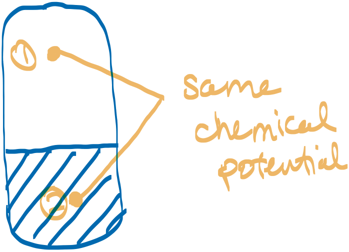


t

chemical potential : μ

for a single substance : $\mu = \frac{G}{n} = G_m$

At equilibrium, the chemical potential of a substance is the same in and throughout every phase present in the system.



consider transferring an infinitesimal amount dn of the substance from one location to another :

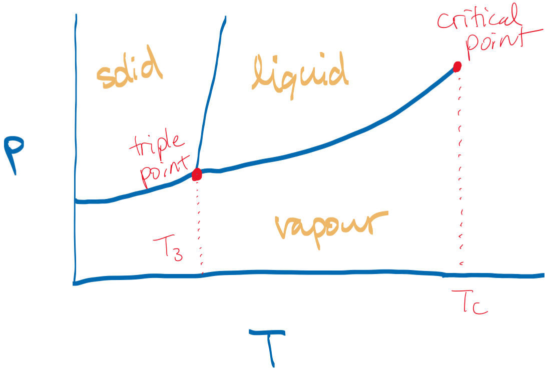
$-\mu_1 dn$

$+\mu_2 dn$

overall: $dG = (\mu_2 - \mu_1)dn$

if $\mu_1 > \mu_2$, this change will be spontaneous

only if $\mu_1 = \mu_2$, then $dG = 0$ and only then is the system at equilibrium.



critical point : surface between liquid and vapour disappears above this temperature

at and above critical point, we

have a supercritical fluid

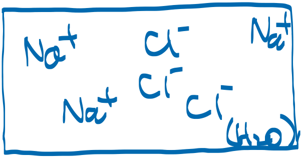
triple point: all three phases are in equilibrium

The Phase Rule

- **variance / number of degrees of freedom**, F: number of intensive variables that can be changed independently without disturbing the number of phases in equilibrium

- **constituent**: any chemical species present

- **component**: chemically independent constituent



3 constituents: Na^+, Cl^-, H_2O

2 components: Na^+/Cl^-, H_2O

Develop the phase rule, 1 component:

$\boxed{P = 1}$, then both p, T can be varied independently; $\boxed{F = 2}$

$\boxed{P = 2}$, two phases α and β

$$\mu(\alpha; p, T) = \mu(\beta; p, T)$$

write p as a function of T

only one independent variable

$\boxed{F = 1}$

$\boxed{P = 3}$

$$\mu(\alpha; p, T) = \mu(\beta; p, T) = \mu(\gamma; p, T)$$

$$\left.\begin{aligned} \mu(\alpha; p, T) &= \mu(\beta; p, T) \\ \mu(\beta; p, T) &= \mu(\gamma; p, T) \end{aligned}\right] \begin{aligned} &\text{two equations} \\ &\text{two variables} \end{aligned}$$

only a single solution exists

$$\boxed{F=0}$$

$\therefore$ When $C=1$: $F=2$ when $P=1$
$F=1$ when $P=2$
$F=0$ when $P=3$

$$\boxed{F=3-P}$$

Generalize to any number of components:

intensive variables: p, T, x ← mole fraction

$$x_A + x_B + x_C + \dots + x_n = 1$$

$C-1$

↑

can be in any phase in the system

$(C-1)P+2$ ← total number of intensive variables

$\mu_J(\alpha; p, T) = \mu_J(\beta; p, T) = \ldots$ for P phases

$P-1$ equations

$C(P-1)$ reductions

$$F = (C-1)P + 2 - C(P-1)$$

$$\boxed{F = C - P + 2}$$ general form of phase rule