ChE Thermodynamics
Quiz 6 February 20, 2020 (2/20/2020)

Egg albumen is a protein from egg whites. In the egg the protein is in a native (folded) state. It is desired to obtain an unfolded protein without degrading the protein through the use of pressure. Albumen can be completely denatured (unfolded) with a pressure of 100 MPa in the absence of significant heat. The protein is destroyed with a temperature of 120°C but it already begins to degrade at 75°C.

Is it possible to heat a closed container of chloroform from $T_1 = 1°C$, $p_1 = 0.1$MPa containing egg albumen to generate 100MPa pressure, thereby denaturing the protein, without heating above 75°C and causing degradation (burning)? Using chloroform as the solvent, how much heat will be required per mole of chloroform. Consider a closed container of constant volume containing only chloroform (ignore the protein). **FILL OUT THE TABLE ON PAGE 3 AND *INCLUDE IT WITH YOUR ANSWERS***

For ***chloroform*** the following data is available:

C_p = 65.8 J/(mole K) = $(\partial H/\partial T)_p$ = T $(\partial S/\partial T)_p$
α_p = 1,270 x 10^{-6} K^{-1} = $1/V\,(\partial V/\partial T)_p$
κ_T = 830 x 10^{-6} MPa^{-1} = $-1/V\,(\partial V/\partial P)_T$
ρ = 1.48 g/cm^3
MW = 119 g/mole
$C_V = (\partial U/\partial T)_V$ = T $(\partial S/\partial T)_V$

a) Calculate T_2 by developing an expression for $(\partial p/\partial T)_V$ in terms of the parameters given above using the triple product rule. Is the proposed process possible using chloroform?

b) Find an expression for C_v using C_p, α_p, κ_T, T_1 = 274 K through an expansion of d$S(T,P)$.
Name the steps you use, e.g. Maxwell Relation; Definition of C_p; Triple Product; etc.
Get the value for C_v for this case *(Use T* = 274 K*; calculate V watch units*).

c) Calculate ΔS, ΔU, Q.

d) Calculate ΔH for this constant volume (isochoric) process.
Name the steps you use, e.g. Maxwell Relation; Definition of C_p; Triple Product; etc.

e) Would it be feasible to reach 100 MPa at a temperature below 70°C using water?

For ***water*** the following data is available:

C_p = 33.6 J/(mole K) = $(\partial H/\partial T)_p$ = T $(\partial S/\partial T)_p$
α_p = 210 x 10^{-6} K^{-1} = $1/V\,(\partial V/\partial T)_p$
κ_T = 490 x 10^{-6} MPa^{-1} = $-1/V\,(\partial V/\partial P)_T$
ρ = 0.998 g/cm^3
MW = 18 g/mole

$$\mu_{JT} \equiv \left(\frac{\partial T}{\partial P}\right)_H \quad \alpha_P \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{-1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \quad \kappa_T \equiv \frac{-1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T$$

$$(\partial S/\partial T)_V = C_V/T \quad C_P \equiv (\partial H/\partial T)_P.$$

Maxwell's Relations

$$dU = TdS - PdV \;\Rightarrow\; -(\partial P/\partial S)_V = (\partial T/\partial V)_S \qquad 6.29$$

$$dH = TdS + VdP \;\Rightarrow\; (\partial V/\partial S)_P = (\partial T/\partial P)_S \qquad 6.30$$

$$dA = -SdT - PdV \Rightarrow\; (\partial P/\partial T)_V = (\partial S/\partial V)_T \qquad 6.31$$

$$dG = -SdT + VdP \Rightarrow\; -(\partial V/\partial T)_P = (\partial S/\partial P)_T \qquad 6.32$$

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_F\left(\frac{\partial y}{\partial F}\right)_x\left(\frac{\partial F}{\partial x}\right)_y = -1}$$

6.15 Triple product rule.

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_F = \left(\frac{\partial x}{\partial z}\right)_F\left(\frac{\partial z}{\partial y}\right)_F}$$

6.16 Chain rule interposing a variable.

$$\boxed{\left(\frac{\partial F}{\partial w}\right)_z = \left(\frac{\partial F}{\partial x}\right)_y\left(\frac{\partial x}{\partial w}\right)_z + \left(\frac{\partial F}{\partial y}\right)_x\left(\frac{\partial y}{\partial w}\right)_z}$$

6.17 The expansion rule.

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_x = 0 \quad \text{and} \quad \left(\frac{\partial x}{\partial y}\right)_y = \infty} \quad \boxed{\left(\frac{\partial x}{\partial x}\right)_y = 1}$$

$dS = (C_v/T)\,dT$; $dH = C_p\,dT$; $dU = C_v\,dT = Q + W_s + W_{EC}$

Thermodynamic Square

-S U V
H A
-p G T

Question		Expression	Value	Units
a)	$(\partial p/\partial T)_V$			MPa/K
	T2			°C
b)	Cv			J/(mole K)
c)	DS			J/(mole K)
	DU			J/mole
	Q			J/mole
d)	DH			J/mole
e)	T2 (100 Mpa) for water			°C

Answers Quiz 6

a) $$\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{1}{V\kappa_T}\right)(V\alpha_p)$$

- Triple Product
- Definition of κ_T
- Definition of α_p

$$= \frac{\alpha_p}{\kappa_T} = \frac{1{,}270\times10^{-6}\,K^{-1}}{830\times10^{-6}\,MPa^{-1}} = 1.53\,\frac{MPa}{K}$$

$$\Delta T = \frac{\Delta p}{\left(\frac{\partial p}{\partial T}\right)_V} = \frac{99.9\,MPa}{1.53\,MPa/K} = 65.3\,K$$

$$T_2 = 1^\circ C + 65.3\,K = 66.3\,^\circ C$$

Process works for chloroform.

b) $$dS(T,p) = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$$ Expansion Rule

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$$ Definition of C_p

$$\begin{array}{ccc} -S & U & V \\ H & & A \\ -p & G & T \end{array}$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p = -V\alpha_p$$

Maxwell Relationship

Definition of α_p

$$dS = \frac{C_p}{T}\,dT + (-V\alpha_p)\,dp$$

Take derivative wrt T at const V to get C_V from definition of C_V

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} = \frac{C_p}{T}\left(\frac{\partial T}{\partial T}\right)_V - V\alpha_p\left(\frac{\partial p}{\partial T}\right)_V$$

identity rule

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$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P = \left(+\frac{1}{VK_T}\right)\left(\alpha_P V\right)$$

Triple Product Rule

Definition of K_T & α_P

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha_P}{K_T}}$$ use later

$$\frac{C_V}{T} = \frac{C_P}{T} - \frac{V\alpha_P^2}{K_T}$$

$$\boxed{C_V = C_P - \frac{VT\alpha_P^2}{K_T}}$$

$$V = \frac{MW}{\rho} = \frac{119\ g/mole}{1.48\ g/cm^3} = 80.4\ \frac{cm^3}{mole}$$

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$$C_V = 65.8\ \frac{J}{mol\,K} - \frac{80.4\ \frac{cm^3}{mole}\ (274K)\left(1.270\times10^{-6}\ K^{-1}\right)^2}{830\times10^{-6}\ MPa^{-1}}$$

$$C_V = 65.8\ \frac{J}{mol\,K} - 42.8\ \frac{J}{mol\,K}$$

$$\boxed{C_V = 23.0\ J/mol\,K}$$

c) Calculate ΔS, ΔU & Q

$$dS = \frac{C_v}{T} dT$$

$$\Delta S = C_v \ln \frac{T_2}{T_1} = 23.0 \frac{J}{mole\,K} \ln \frac{(66.3^\circ C + 273\,K)}{(1^\circ C + 273\,K)}$$

$$\boxed{\Delta S = 4.92 \frac{J}{mole\,K}}$$

$$dU = C_v dT$$
$$\Delta U = C_v \Delta T$$
$$= 23.0 \frac{J}{mol\,K} (66.3^\circ C - 1^\circ C)$$

$$\boxed{\Delta U = 1{,}500 \frac{J}{mole}}$$

$$\Delta U = Q + \cancel{W_{EC}}^{0} + \cancel{W_S}^{0}$$
$$\Delta V = 0$$

$$\boxed{Q = 1{,}500\ J/mole}$$

d) $\left(\frac{\partial H}{\partial T}\right)_V$ Needed (not C_p)

$-S$ U V
H A
$-p$ G T

$dH = TdS + VdP$ from Square

Take partial derivative with T at constant V

$$\left(\frac{\partial H}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha_P}{\kappa_T} \text{ Part (b) above}$$

$$\boxed{\left(\frac{\partial H}{\partial T}\right)_V = C_V + \frac{\alpha_P}{K_T} V}$$

$$\left(\frac{\partial H}{\partial T}\right)_V = 23.0 \frac{J}{mole\,K} + \frac{1{,}270 \times 10^{-6}\ K^{-1}}{830 \times 10^{-6}\ MPa^{-1}}\ 80.4 \frac{cm^3}{mole}$$

$$\left(\frac{\partial H}{\partial T}\right)_V = 146 \frac{J}{mole\,K}$$

$$\Delta H = \left(\frac{\partial H}{\partial T}\right)_V \Delta T = 146 \frac{J}{mole\,K} (65.3\ K)$$

$$\boxed{\Delta H = 9{,}540 \frac{J}{mole}}$$

e)

$$\Delta T_{water} = \frac{\Delta P}{\alpha_P / K_T} = \frac{99.9\ MPa}{(210 \times 10^{-6}\ K^{-1} / 490 \times 10^{-6}\ MPa^{-1})}$$

from part (a)

$$= \frac{99.9\ MPa}{0.429\ \frac{MPa}{K}}$$

$$\Delta T_{water} = 233\ K$$

$$\boxed{T_2 = 234\ °C}$$

Protein has burned
Not Feasible

Question		Expression	Value	Units
a)	$(\partial p/\partial T)_V$	α_p/κ_T	1.53	MPa/K
	T2	$\frac{\Delta P}{(\partial P/\partial T)_V} + T_1 = \frac{\Delta P}{\alpha_p/\kappa_T} + T_1$	63.3	°C
b)	Cv	$C_V = C_p - \frac{VT\alpha_p^2}{\kappa_T}$	23.0	J/(mole K)
c)	DS	$C_V \ln \frac{T_2}{T_1}$	4.92	J/(mole K)
	DU	$C_V \Delta T$	1,500	J/mole
	Q	$Q = \Delta U$	1,500	J/mole
d)	DH	$\Delta T\left(C_V + \frac{\alpha_p}{\kappa_T} V\right)$	9,540	J/mole
e)	T2 (100 Mpa) for water	$T_1 + \frac{\Delta P}{\alpha_p/\kappa_T}$	234	°C