Chemistry 553

Hour exam 1

11 February 2011

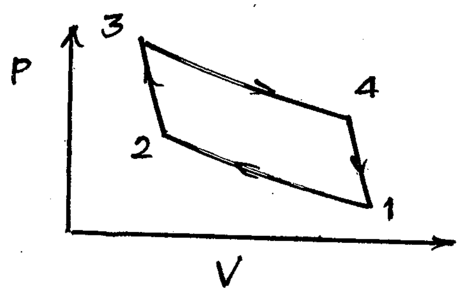
1. (20 pts) State the First and Second Laws of Thermodynamics as they pertain to the system and to the universe.

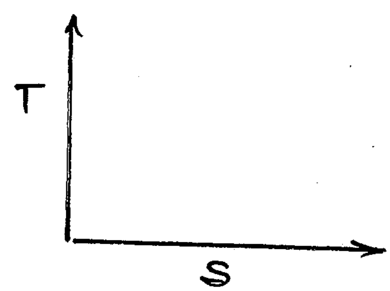
2. (25 pts) Shown is the Carnot cycle in the PV plane (recall: two adiabatic and two isothermal steps).

   (a) Plot T vs S labelling the points $1 \cdots 4$ consistent with the PV plot.

   (b) Calculate $\oint dq, \oint dw$ for the cycle.

   (c) Which step extracts heat from the surroundings?





3. (20 pts) We will consider two routes to the specification of X and Y in the equation,

$$dS(T, V) = XdT + YdV \tag{1}$$

First, insert $dP(T, V)$ into

$$dS(T, P) = \frac{C_p}{T}dT - \alpha_p V dP \tag{2}$$

and in so doing, derive an equation for $dS(T, V)$ which is expressed in terms of C_v and various derivatives of the equations of state.

Next, compare your result for $dS(T, V)$ with that derived directly.

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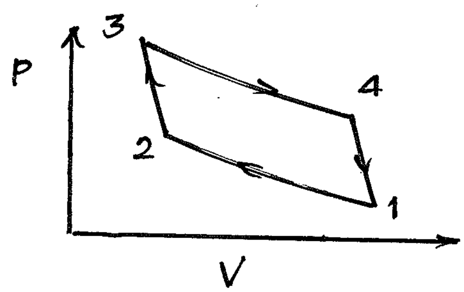

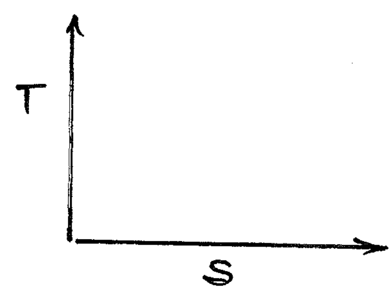

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4. (15 pts) A system with two states has a Helmholtz energy

$$\frac{A(N,T,x_1)}{N} = x_1\epsilon + k_B T \left(x_1 \ln x_1 + x_2 \ln x_2\right) \tag{3}$$

where x_i is the mole fraction of component i, and ϵ is the energy of component 1. Minimize the free energy, subject to constraints, and derive the ratio, $K(T) = \frac{x_1}{x_2}$.

5. (20 pts) Consider a two state model for polymer folding in which there is a single folded state of energy $-\epsilon$ ($\epsilon > 0$) and an m-fold degenerate unfolded state of zero energy.

   (a) Calculate $\Delta A = A_{folded} - A_{unfolded}$, and the temperature at which the transition from folded to unfolded occurs.

   (b) Plot $A(T)$ vs T for both forms of the polymer, folded and unfolded, indicating the folded and unfolded branches and the crossing at the transition temperature.

Exam 1

1. First law

$$\Delta U|_{univ} = 0$$

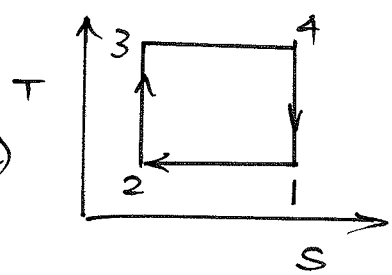
$$\Delta U|_{sys} = \underbrace{q_{by}}_{\text{heat absorbed by the system}} + W_{on}$$ work done on the system

Second law

$$\Delta S|_{univ} \geq 0$$ entropy increases for spontaneous processes.

$$\Delta S|_{sys} \geq q_{by}/T$$ where the equality describes reversible processes

2. a)



b) $\oint dq + \oint dw = \oint dU = 0$

$$\oint dq = q(1\to2) + q(3\to4)$$

$$\Delta U(1\to2) = 0 = q(1\to2) - \int_{V_1}^{V_2} RT\,dV/V$$

$$q(1\to2) = T_1 R \ln(V_2/V_1)$$

$$q(3\to4) = RT_3 \ln(V_4/V_3)$$

But the two adiabatic steps share the same two isothermals, so $\frac{V_1}{V_4} = \frac{V_2}{V_3} \Rightarrow \frac{V_2}{V_1} = \frac{V_3}{V_4}$

$$q(1\to2) + q(3\to4) = R(T_1 - T_3)\ln(V_2/V_1)$$

$$\oint dw_{by} = \oint dq_{by}$$

c) $3 \rightarrow 4$ extracts heat.

3.

a) $$dS = \frac{C_P}{T}\,dT - \alpha_P V\,dP$$

but $$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

$$dS = \frac{C_P}{T}\,dT - \alpha_P V\left\{\left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV\right\}$$

$$= \left[\frac{C_P}{T} - \left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V\right] dT - \underbrace{\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial V}\right)_T}_{\left(\frac{\partial P}{\partial T}\right)_V} dV$$

so

$$dS = \left[\frac{C_P}{T} - \left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V\right] dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

b)

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

C_V/T

$dA = -SdT - pdV$

so, $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

and $$dS = \frac{C_V}{T}\,dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$\therefore \quad C_V = C_P - T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V$$

4. $\frac{A}{N} = x_1 \epsilon + k_B T \left[x_1 \ln x_1 + x_2 \ln x_2 \right]$

can replace $x_2 = 1 - x_1$ and diff wrt x_1 or use Lagrangian multipliers.

$$\frac{dA}{dx_1} = 0 = \epsilon + k_B T \left\{ \ln x_1 + 1 - [\ln x_2 + 1] \right\}$$

or

$$\beta \epsilon + \ln (x_1 / x_2) = 0$$

and

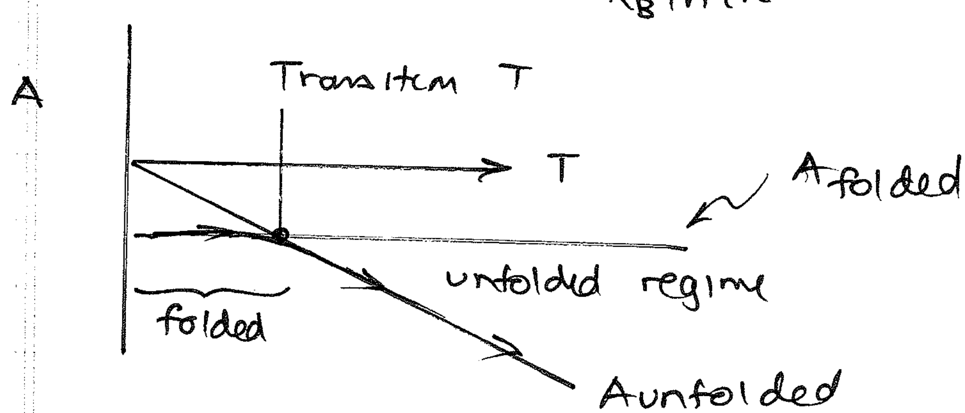
$$\frac{x_2}{x_1} = e^{\beta \epsilon}, \quad \text{or} \quad K(T) = \frac{x_1}{x_2} = e^{-\beta \epsilon}$$

5. $A_{folded} = -\epsilon$

$A_{unfolded} = -k_B T \ln m$

$\Delta A = -\epsilon + k_B T \ln m$, The T @ which folding occurs is

$$k_B T \ln m = \epsilon$$
$$T = \frac{\epsilon}{k_B \ln m}$$



arrows are the direction (or path nature takes in minimizing A).