10.40 Thermodynamics **Fall 2003**

Problem Set 3

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a) For the plane with two tangent points in Fig. 5.2b, estimate the value of *G, H, A, U,* and *S* of each phase. Obviously, the grids are course, and difficult to read, so the key is to make all of the values of the thermodynamic properties consistent.

b) Explain the significance of a *USV* surface, like the one on Figure 5.1, but with a plane with 4 points of tangency.

Solution:

a.) There are two ways to solve this problem, and one way is more accurate than the other. For each phase, U, S and V can be read directly from the chart. The problem lies in calculating G, H, and A in a way that makes all the thermodynamic properties consistent.

A, H and G can be calculated from the functional equations (Table 5.2 in T&M) that are obtained by Euler integration of the fundamental equation after one (or two) Legendre transforms. Since we are working with a closed system and are using intensive variables:

$$H = U + PV \tag{1}$$

$$A = U - TS \tag{2}$$

$$G = U + PV - TS \tag{3}$$

Since the two points are tangent to the same plane on the USV surface for pure ethylene, we know that they represent two phases in equilibrium. Therefore, the phases are at the same temperature, T, and pressure, P. Likewise, since the phases are in equilibrium, the molar Gibbs free energy, G, for each system must be equal. (Remember that G = μ for a single component simple system). This is equivalent to saying that all points on the plane have the same molar Gibbs free energy. Therefore, we can also determine G from the USV surface by reading the value of U where the plane intercepts the U axis and V = S = 0. This can be seen directly from equation (3).

The values for each point as determined from the chart are given in the table below. Obviously, it is difficult to read this chart, so the numbers below can only be taken as a rough estimate.

	Point 1	**Point 2**	**Intersection of Plane with U/RT_c axis**
U/RT_c	-8.2	-4.3	-1.1
S/R	-7.7	-3.2	0
V/V_c	0.8	5.8	0

For ethylene:
T_c = 282.34 K
V_c = 0.132 m^3/kmol = 0.132 * 10^{-3} m^3/mol
R = 8.314 J/(mol K)

Substituting these into the expressions in the table above, we get:

	Point 1	**Point 2**	**Intersection of Plane with U/RT_c axis**
U (J/mol)	-19248	-10094	-2580
S (J/mol K)	-64.0	-26.6	0
V *10^3 (m^3/mol)	0.106	0.7656	0
G (J/mol)	-2580	-2580	-2580

Now our problem is determining T and P for the points, so that A and H can be calculated. There are two ways to do this. The first way comes from applying equation (3) to each point:

$$\begin{aligned} G_1 - U_1 &= PV_1 - TS_1 \\ G_2 - U_2 &= PV_2 - TS_2 \end{aligned} \tag{4}$$

Since the values for each G, U, V and S are known from the chart, and P & T are the same for each point since they are in equilibrium, we are left with two equations in two unknowns. Solving them simultaneously, we get
T = 259 K
P = 8.15 x 10^5 Pa or 8.15 bar

These values can then be plugged into equations (1) and (2) to determine A and H. The results are shown in the table below.

	Point 1	**Point 2**
G (J/mol)	-2580	-2580
U (J/mol)	-19248	-10094
S (J/mol K)	-64.0	-26.6
V *10^3 (m^3/mol)	0.106	0.7656
H (J/mol)	-19162	-9471
A (J/mol)	-2667	-3205

The second method comes from the total differential for U. Since:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV = TdS - PdV \tag{5}$$

$$T = \left(\frac{\partial U}{\partial S} \right)_V$$
$$P = -\left(\frac{\partial U}{\partial V} \right)_S \tag{6}$$

Therefore, T and P can be estimated by calculating the change in U with S at constant V and the change in U with V at constant S, respectively, for the plane. Using this method, it was estimated that:
T = 236 K
P = 12.3 bar

To ensure that all thermodynamic properties were consistent, G was calculated for points 1 and 2 using equation (3), the USV data in the first table, and the newly estimated T and P. It was found that:
G_1 = -2900 J/mol
G_2 = -4000 J/mol

Remember that since the phases are in equilibrium, G_1 and G_2 should be equal. The calculated values and the one determined from the chart are in pretty good agreement, so the values of T and P calculated must be fairly accurate. The difference is obviously due to errors from reading the chart, especially since U does not vary much for the plane along a constant S line. Because of this, it is recommended that that first method discussed be used instead.

(b)
A USV plane with 4 points of tangency implies that:

1.) there are 4 phases in equilibrium, and
2.) the system is made up of 2 or more components, since a 1 component system can have at most 3 phases in equilibrium (the triple point).

No more information can be derived from the described surface without actually seeing it.