10.40 Thermodynamics **Fall 2003**
Exam 1

Problem 1

1. (40 points) This is a 6 part problem worth a total of 40 points

(a) (6 points) If for a given system, closed, with one component, we had a function $A=A(U,T)$, could this function contain the equivalent amount of information as the fundamental equation for intensive properties? Briefly explain your answer.

(b) (6 points) Express the following derivative in terms of measurable properties for a single component: $\left(\frac{\partial G}{\partial A}\right)_T$.

(c) (6 points) Express $y^{(k)} = f(P, \underline{S}, N_A, \mu_B, N_C, ...)$ in terms of a Legendre transform of $\underline{H}$ = $y^{(0)}$ for an n component system. Also express the total differential, $dy^{(k)}$, in terms of derived and primitive thermodynamic properties.

(d) (10 points) Are there restrictions on the signs of C_p and α_p for any real, single component system? Explain your answer.

(e) (6 points) For a system containing 5 components, considering only intensive properties, how many dimensions does the Gibbs surface have, not including the U dimension? Explain the significance of a plane tangent to the Gibbs surface at two points.

(f) (6 points) Express $\underline{G}_{PT}$ in terms of derivatives of $\underline{H}$ for an n component system.

Solution:
(a)
No, the function A=A(U,T) cannot contain the equivalent amount of information as the fundamental equation. If we could, then we could envision some Legendre transform that would take us from the fundamental equation, $y^{(0)}$ = S = f(U, V) to $y^{(k)}$ = A = f(U, T). A quick inspection shows that $y^{(1)}$ = f(1/T, V) or $y^{(1)}$ = f(U, P) or $y^{(2)}$ = f(1/T, P). We conclude that a Legendre transform to $y^{(k)}$ = A = f(U, T) is not possible because V and T would have to be conjugate pairs to make the transformation. One could also say that U and 1/T are a conjugate pair, and thus they can not be varied independently without changing the original form (and thus the information content) of the fundamental equation. For example, for an ideal gas, U=U(T) only. Therefore, A=A(U,T)=A(T) and could not possibly contain the same information as the fundamental equation since it only depends on a single variable.

It could also be shown that the total derivative of A=A(U,T) can only be integrated to within an arbitrary constant of the original fundamental equation, and therefore does not contain the same information.

An alternative way to solve this problem is to look at the Legendre transform of A in terms of U.

$$A = U - TS$$

$$dU = TdS - PdV$$

$$dA = dy^{(1)} = \underbrace{TdS - PdV}_{dU}\underbrace{-TdS - SdT}_{-d(TS)}$$

From the expressions for A and dA, we see that we need both U and the *procuct* of TS to completely characterize A, not just U and T.

(b)

There are several ways to express $(\partial G/\partial A)_T$ in terms of measurable properties.

Long method:

$$G = A + PV$$

$$\left(\frac{\partial G}{\partial A}\right)_T = \left(\frac{\partial(A+PV)}{\partial A}\right)_T = \underbrace{\left(\frac{\partial A}{\partial A}\right)_T}_{=1} + P\left(\frac{\partial V}{\partial A}\right)_T + V\left(\frac{\partial P}{\partial A}\right)_T$$

$$\left(\frac{\partial V}{\partial A}\right)_T = \left(\left(\frac{\partial A}{\partial V}\right)_T\right)^{-1} = (-P)^{-1} = -\frac{1}{P}$$

$$\left(\frac{\partial P}{\partial A}\right)_T = \left(\left(\frac{\partial A}{\partial P}\right)_T\right)^{-1} = \left(-S\underbrace{\left(\frac{\partial T}{\partial P}\right)_T}_{=0} - P\left(\frac{\partial V}{\partial P}\right)_T\right)^{-1} = \left(-P\left(\frac{\partial V}{\partial P}\right)_T\right)^{-1}$$

Substituting into the original equation gives

$$\left(\frac{\partial G}{\partial A}\right)_T = 1 - \frac{P}{P} - \frac{V}{P}\left(\frac{\partial P}{\partial V}\right)_T$$

$$\left(\frac{\partial G}{\partial A}\right)_T = -\frac{V}{P}\left(\frac{\partial P}{\partial V}\right)_T$$

Shorter method:

Add another variable to the original derivative:

$$\left(\frac{\partial G}{\partial A}\right)_T = \frac{\left(\partial G/\partial V\right)_T}{\left(\partial A/\partial V\right)_T}$$

$$\left(\partial G/\partial V\right)_T = \left(\partial G/\partial P\right)_T\left(\partial P/\partial V\right)_T = V\left(\partial P/\partial V\right)_T$$

$$\left(\partial A/\partial V\right)_T = -P$$

$$\left(\frac{\partial G}{\partial A}\right)_T = -\frac{V}{P}\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{P}\left(-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T\right)^{-1} = \frac{1}{P\kappa_T}$$

Shortest Method:
Substitute differential forms into numerator and denominator

$$\left(\frac{\partial G}{\partial A}\right)_T = \left(\frac{\overbrace{-S\partial T}^{=0 \text{ at const T}} + V\partial P}{\underbrace{-S\partial T}_{=0 \text{ at const T}} - P\partial V}\right)_T = -\frac{V}{P}\left(\frac{\partial P}{\partial V}\right)_T$$

(c)
First, re-order:
$y^{(0)} = \underline{H} = f(N_B, \underline{S}, P, N_A, N_C, \ldots)$
$y^{(k)} = f(\mu_B, \underline{S}, P, N_A, N_C, \ldots)$

$y^{(0)}$: x_i	$y^{(0)}$: ξ_i	$y^{(k)}$: x_i	$y^{(k)}$: ξ_i
N_B	μ_B	μ_B	$-N_B$
$\underline{S}$	T	$\underline{S}$	T
-P	$-\underline{V}$	-P	$-\underline{V}$
N_A	μ_A	N_A	μ_A
N_C	μ_C	N_C	μ_C
:	:	:	:

From Equation (5-91) in the text, with respect to the table for $y^{(0)}$:

$$y^{(k)} = y^{(0)} - \sum_{i=1}^{k} \xi_i x_i$$

For our case, k = 1 and

$$y^{(k)} = y^{(1)} = \underline{H} - \mu_B N_B$$

From Equation (5-93) in the text, with respect to the table for $y^{(0)}$:

$$dy^{(k)} = -\sum_{i=1}^{k} x_i d\xi_i + \sum_{i=k+1}^{m} \xi_i dx_i$$

$$dy^{(k)} = dy^{(1)} = -N_B d\mu_B + Td\underline{S} + \underline{V}dP + \mu_A dN_A + \mu_C dN_C + \ldots\mu_n dN_n$$

(d)
By definition:

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{P,N} = \frac{T}{N}\left(\frac{\partial \underline{S}}{\partial T}\right)_{P,N} \qquad \alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N} = \frac{1}{\underline{V}}\left(\frac{\partial \underline{V}}{\partial T}\right)_{P,N}$$

Therefore, the question becomes, are there any restrictions on the signs of either $(\partial S/\partial T)_P$ or $(\partial V/\partial T)_P$ for a real, single component system? The only way in which there could be restrictions on these derivatives would be if there existed some criteria of stability which prevented the derivatives from obtaining a certain sign for a stable system. From Chapter 7, assuming that $y^{(0)} = \underline{U} = f(\underline{S}, \underline{V}, N)$, we are told that the necessary conditions for a stable system are:

$y_{kk}^{(k-1)} > 0$, k = 1, 2, ..., m-1 where m = n+2, n = # of components Eq. (7-12)

Moreover, we are told that the necessary and sufficient criterion of stability is that

$y_{(m-1)(m-1)}^{(m-2)} > 0$, with m $\equiv$ n + 2 Eq. (7-15)

For our case, n = 1 and m = 3. From Eq. (7-12), all the necessary conditions for a stable system can be represented by two expressions:

$y_{11}^{(0)} > 0$ and $y_{22}^{(1)} > 0$

Note: $y_{22}^{(3)} = G_{TT}$ or $G_{PP} > 0$ is **not** a valid stability criterion since we are working with a 1-component system.

From these two expressions, for our n = 1 component system, a total of 9 expressions can be formed, 6 from the $y^{(1)}$ form of the necessary conditions:

Image removed due to copyright considerations. Please see Tester, J. W., and Michael Modell. *Thermodynamics and Its Applications.* Upper Saddle River, NJ: Prentice Hall PTR, 1997, p. 210, Table 7.1.

and 3 from the $y^{(0)}$ form of the necessary conditions:

$$y_{11}^{(0)} = \underline{U}_{\underline{S}\underline{S}} = \left(\frac{\partial T}{\partial \underline{S}}\right)_{\underline{V},N}$$

$$y_{11}^{(0)} = \underline{U}'_{\underline{V}\underline{V}} = -\left(\frac{\partial P}{\partial \underline{V}}\right)_{\underline{S},N}$$

$$y_{11}^{(0)} = \underline{U}''_{NN} = \left(\frac{\partial \mu}{\partial N}\right)_{\underline{S},\underline{V}}$$

For C_P, looking at Table 7.1, we quickly see that

$$y_{22}^{(1)} = \underline{H}_{\underline{S}\underline{S}} = \left(\frac{\partial T}{\partial \underline{S}}\right)_{P,N} = \left(\frac{NC_P}{T}\right)^{-1} > 0$$

and since N and T are always positive, we conclude that $C_P > 0$ always.

Another option some students used was to start with Eq. (8-143)

$$C_P = C_V + \frac{TV\alpha_P^2}{\kappa_T}$$

and show that $C_V = N^{-1}(\partial \underline{S}/\partial T)_{\underline{V},N} = (N\underline{U}_{SS})^{-1} > 0$. Also T and V > 0 always, as is $\kappa_T = -\underline{V}^{-1}(\partial \underline{V}/\partial P)_{T,N} = (-\underline{V}\,\underline{U}_{SS})^{-1}$. And since $\alpha_P^2 > 0$, then $C_P > 0$ always as well.

For α_P, scanning our list of necessary conditions, we do not see any limitations on $(\partial \underline{V}/\partial T)_{P,N}$. Therefore, we conclude that α_P can take on either positive or negative values. Common experience also tells us this. For example, the majority of gases expand when they are heated at a constant pressure – this is how hot air balloons are able to float. However, liquid water expands as it is cooled from about 4°C to 0°C – this is why ice floats in water. This shows how α_P can have both positive and negative values.

(e)
The first postulate states that a simple system at equilibrium can be described by *n*+2 independent variables, where *n* is the number of components in the system. However, we are only concerned with the *intensive* properties of the system. As stated in Chapter 5 of the text, a corollary to the 1st postulate is that for a single phase simple system, there are *n*+1 independently variable intensive properties. Therefore, the Gibbs surface has *n*+1 = 6 dimensions, not including the U dimension. For example, we could have $U=U(S, V, x_1, x_2, x_3, x_4)$. The Gibbs surface would have 7 dimensions in all: one dimension would be *U*, and the 6 others would be the 6 independently variable intensive properties of which *U* is a function.

A plane tangent to two points of a Gibbs surface indicates that there are 2 phases present, and that these phases are in equilibrium ($T_\alpha = T_\beta, P_\alpha = P_\beta, V_\alpha = V_\beta, \mu_{i\alpha} = \mu_{i\beta}$). Each of the phases could contain anywhere between 1 and 5 of the components in the system.

(f)
This question was not well worded, and as a result a large number of answers that were technically correct were accepted. The only requirement was that the solution be in terms of $\underline{H}$ and its derivatives.

The simplest method was to use the tables given in the book. If we define $\underline{G}$ such that $\underline{G} = y^{(1)} = f(T, P, N_i)$, then

$$\underline{G}_{PT} = \left(\frac{\partial}{\partial T}\left(\frac{\partial \underline{G}}{\partial P}\right)_T\right)_P = y_{21}^{(1)} = y_{12}^{(1)} \text{ by the Maxwell relations.}$$

Noting that G is the 1st Legendre transform of $y^{(0)} = \underline{H} = f(\underline{S}, P, N_i)$ with respect to $\underline{S}$, we see from Table 5.3, Equation (5-119) that:

$$y_{12}^{(1)} = \frac{y_{12}^{(0)}}{y_{11}^{(0)}} = \frac{\underline{H}_{\underline{S},P}}{\underline{H}_{\underline{S},\underline{S}}} = \frac{\left(\frac{\partial}{\partial P}\left(\frac{\partial \underline{H}}{\partial \underline{S}}\right)_{P,N}\right)_{\underline{S},N}}{\left(\frac{\partial}{\partial \underline{S}}\left(\frac{\partial \underline{H}}{\partial \underline{S}}\right)_{P,N}\right)_{P,N}}$$

Noting that $(\partial H/\partial \underline{S})_{P,N} = T$, we have

$$\underline{G}_{PT} = \frac{\left(\partial T/\partial P\right)_{\underline{S},N}}{\left(\partial T/\partial \underline{S}\right)_{P,N}}$$

Another accepted solution was reached by simply noting that

$$\underline{G}_{PT} = \left(\frac{\partial}{\partial T}\left(\frac{\partial \underline{G}}{\partial P}\right)_T\right)_P$$

$$\left(\frac{\partial \underline{G}}{\partial P}\right)_{T,N} = \underline{V} = \left(\frac{\partial \underline{H}}{\partial P}\right)_{\underline{S},N}$$

$$\underline{G}_{PT} = \left(\frac{\partial}{\partial T}\left(\frac{\partial \underline{H}}{\partial P}\right)_{\underline{S},N}\right)_{P,N}$$

Along the same lines, it could be argued that

$$\underline{G}_{PT} = \left(\frac{\partial \underline{V}}{\partial T}\right)_{P,N} = \left(\frac{\partial \underline{V}/\partial \underline{H}}{\partial T/\partial \underline{H}}\right)_{P,N} = \frac{\left(\partial \underline{H}/\partial \underline{V}\right)_{P,N}}{\left(\partial \underline{H}/\partial T\right)_{P,N}}$$

Conversely, one could take the derivative of $\underline{G}$ w.r.t. T first (by Maxwell) and get many different answers:

$$\underline{G}_{TP} = \left(\frac{\partial}{\partial P}\left(\frac{\partial \underline{G}}{\partial T}\right)_{P,N}\right)_{T,N} = -\left(\frac{\partial \underline{S}}{\partial P}\right)_{T,N}$$

Using the triple product rule:

$$-\left(\frac{\partial \underline{S}}{\partial P}\right)_T = \left(\frac{\partial T}{\partial P}\right)_{\underline{S},N}\left(\frac{\partial \underline{S}}{\partial T}\right)_{P,N}$$

$$T = \left(\frac{\partial \underline{H}}{\partial \underline{S}}\right)_{P,N}$$

$$\left(\frac{\partial \underline{S}}{\partial T}\right)_{P,N} = \frac{N}{T}C_P = \frac{1}{T}\left(\frac{\partial \underline{H}}{\partial T}\right)_{P,N}$$

$$-\left(\frac{\partial \underline{S}}{\partial P}\right)_T = \left(\frac{\partial}{\partial P}\left(\frac{\partial \underline{H}}{\partial \underline{S}}\right)_{P,N}\right)_{\underline{S},N} \frac{1}{T}\left(\frac{\partial \underline{H}}{\partial T}\right)_{P,N} = \frac{\underline{H}_{SP}}{T}\left(\frac{\partial \underline{H}}{\partial T}\right)_{P,N}$$

Where T is given in terms of H above.

Likewise, one could also start with $\underline{G}_{TP}$ and realize that

$$\underline{G}_{TP} = -\left(\frac{\partial \underline{S}}{\partial P}\right)_{T,N}$$

$$\left(\frac{\partial \underline{H}}{\partial P}\right)_{T,N} = T\left(\frac{\partial \underline{S}}{\partial T}\right)_{T,N} + \underline{V}$$

$$\underline{G}_{TP} = -\left(\frac{\partial \underline{S}}{\partial T}\right)_{T,N} = \frac{-1}{T}\left(\frac{\partial \underline{H}}{\partial P}\right)_{T,N} + \frac{\underline{V}}{T}$$

Where V and T are described in terms of H above.

Finally, if one had a lot of time on their hands during the test, they could start from

$$\underline{G} = \underline{H} - T\underline{S}$$

$$\left(\frac{\partial \underline{G}}{\partial P}\right)_{T,N} = \left(\frac{\partial \underline{H}}{\partial P}\right)_{T,N} - T\left(\frac{\partial \underline{S}}{\partial P}\right)_{T,N} - \underline{S}\underbrace{\left(\frac{\partial T}{\partial P}\right)_{T,N}}_{=0}$$

$$\left(\frac{\partial}{\partial T}\left(\frac{\partial \underline{G}}{\partial P}\right)_{T,N}\right)_{P,N} = \left(\frac{\partial}{\partial T}\left(\frac{\partial \underline{H}}{\partial P}\right)_{T,N}\right)_{P,N} - \left(\frac{\partial}{\partial T}\left(T\left(\frac{\partial \underline{S}}{\partial P}\right)_{T,N}\right)\right)_{P,N}$$

$$\underline{G}_{TP} = \left(\frac{\partial}{\partial T}\left(\frac{\partial \underline{H}}{\partial P}\right)_{T,N}\right)_{P,N} + \left(\frac{\partial}{\partial T}\left(T\left(\frac{\partial \underline{V}}{\partial T}\right)_{P,N}\right)\right)_{P,N}$$

$$\underline{G}_{TP} = \left(\frac{\partial}{\partial T}\left(\frac{\partial \underline{H}}{\partial P}\right)_{T,N}\right)_{P,N} + \left(\frac{\partial \underline{V}}{\partial T}\right)_{P,N} + T\left(\frac{\partial^2 \underline{V}}{\partial T^2}\right)_{P,N}$$

where V is described in terms of H above.