

Additional Notes and Solution Manual For: Thermodynamics by Enrico Fermi

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August 1, 2014

Introduction

Here you'll find some notes that I wrote up as I worked through this excellent book. I've worked hard to make these notes as good as I can, but I have no illusions that they are perfect. If you feel that there is a better way to accomplish or explain an exercise or derivation presented in these notes; or that one or more of the explanations is unclear, incomplete, or misleading, please tell me. If you find an error of any kind – technical, grammatical, typographical, whatever – please tell me that, too. I'll gladly add to the acknowledgments in later printings the name of the first person to bring each problem to my attention.

Acknowledgments

Special thanks to (most recent comments are listed first): Neill Warrington, Eduardo Becerra, Giacomo Caria, Rosario Oliva, Juanico Loran, Glenn Musano, and Don Rintala for helping improve these notes and solutions.

All comments (no matter how small) are much appreciated. In fact, if you find these notes useful I would appreciate a contribution in the form of a solution to a problem that is not yet worked in these notes. Sort of a “take a penny, leave a penny” type of approach. Remember: pay it forward.

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Addendums/Clarifications/Derivations

Constraints on Motion in the p - V plane (Page 6)

Note that in general, there is no conditions or requirements on the motion of a piston in connection with the gas to which it is attached. What this means is that without any other information the path in (V, p) can be taken arbitrary and simply represents the projection of points in (V, p, T) space onto the (V, p) plane. The only requirement is that at every (V, p) point the gas is assumed to be in equilibrium and must satisfy its equation of state $f(p, V, T) = 0$. In this way the temperature T maybe computed if desired.

If we are told more information about the specific type of path in the (V, p) plane (like in fact that it is along an *isentrop*e or an *isotherm*) then the path in the (V, p) plane is completely specified by its two endpoints.

Equivalence of the Pressure and Volume Formulation of the Work done during an Isothermal Expansion (Page 9)

Now p_1 and p_2 are the initial and final pressures for m grams of an ideal gas under an isothermal expansion. As such evaluating the ideal gas law at the two end points gives

$$p_1 V_1 = \frac{m}{M} RT \quad (1)$$

$$p_2 V_2 = \frac{m}{M} RT \quad (2)$$

where T the common temperature. Dividing these two expressions we have

$$\frac{p_1 V_1}{p_2 V_2} = 1 \quad (3)$$

or separating volume and pressure to alternate sides of the equation give

$$\frac{V_1}{V_2} = \frac{p_2}{p_1}. \quad (4)$$

It is because of this relationship that we have the equivalence of the two work expressions given in Fermi Eq. 10 from the book.

The Derivation of the change in Heat Q in terms of the Variables T and p (Page 20)

The first law of thermodynamic in terms of its “canonical” variables U and V is given by

$$dU + pdV = dQ.$$

To express this in terms of the independent variables T and p we first express the differential of internal energy U in terms of these variables (using standard calculus) as

$$dU = \left(\frac{\partial U}{\partial p}\right)_T dp + \left(\frac{\partial U}{\partial T}\right)_p dT. \quad (5)$$

In the same way, we next express the differential of V in terms of the variables T and p as

$$dV = \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT. \quad (6)$$

These two expressions are then inserted into the left hand side of the first law of thermodynamics (replacing dU and dV) giving

$$\left(\frac{\partial U}{\partial p}\right)_T dp + \left(\frac{\partial U}{\partial T}\right)_p dT + p \left[\left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT \right] = dQ. \quad (7)$$

Now grouping dp and dT terms we obtain

$$\left[\left(\frac{\partial U}{\partial p}\right)_T + p \left(\frac{\partial V}{\partial p}\right)_T \right] dp + \left[\left(\frac{\partial U}{\partial T}\right)_p + p \left(\frac{\partial V}{\partial T}\right)_p \right] dT = dQ. \quad (8)$$

Which is Fermi Eq. 23.

Expressions Relating the Change in Q to the Specific Heats C_p and C_V (Page 24)

Now Fermi Eq. 30 is

$$C_V dT + p dV = dQ, \quad (9)$$

and taking the differential of the ideal gas law gives (Fermi Eq. 31) or

$$p dV + V dp = R dT. \quad (10)$$

When Eq. 9 is subtracted from Eq. 10 we obtain

$$C_V dT - V dp = dQ - R dT, \quad (11)$$

or grouping all coefficients of dT we obtain

$$(C_V + R) dT - V dp = dQ. \quad (12)$$

This is Fermi Eq. 32. Now a transformation at constant pressure has $dp = 0$ (by definition) and remembering the definition of C_p

$$C_p \equiv \left(\frac{dQ}{dT}\right)_p,$$

we obtain from Eq. 12

$$C_p = \left(\frac{dQ}{dT} \right)_p = C_V + R. \quad (13)$$

Which is Fermi Eq. 33. As described in the text this same expression can be obtained for a ideal gas in the following way. Since for an ideal gas the internal energy U is only a function of only T the partial derivative holding p constant becomes a total derivative

$$\left(\frac{\partial U}{\partial T} \right)_p = \frac{dU}{dT} = C_V. \quad (14)$$

Because we know that the general relationship between C_p and C_V is given by

$$C_p = \left(\frac{dQ}{dT} \right)_p = \left(\frac{dU}{dT} \right)_p + p \left(\frac{dV}{dT} \right)_p. \quad (15)$$

Which for an ideal gas and Eq. 14 becomes

$$C_p = C_V + p \frac{\partial}{\partial T} \left(\frac{RT}{p} \right)_p = C_V + p \frac{R}{p} = C_V + R. \quad (16)$$

Which again is Fermi Eq. 33. For a monotonic gas with $C_V = \frac{3}{2}R$ the above gives

$$C_p = \frac{3}{2}R + R = \frac{5}{2}R \quad (17)$$

For a diatomic gas (with $C_V = \frac{5}{2}R$) the above calculation becomes

$$C_p = \frac{5}{2}R + R = \frac{7}{2}R. \quad (18)$$

From the definition of $K = \frac{C_p}{C_V}$ and the fact that $C_p = C_V + R$ we see that

$$K = 1 + \frac{R}{C_V} \quad (19)$$

For a monotonic gas with $C_V = \frac{3}{2}R$ we have that

$$K = 1 + \frac{R}{\frac{3}{2}R} = 1 + \frac{2}{3} = \frac{5}{3} \quad (20)$$

In the exact same way a diatomic gas has

$$K = 1 + \frac{R}{\frac{5}{2}R} = 1 + \frac{2}{5} = \frac{7}{5}, \quad (21)$$

for its ratio of specific heats.

Constraints on p , V , and T under an Adiabatic Transformations of an Ideal Gas (Page 25-26)

For an adiabatic transformation $dQ = 0$ and from Eq. 9 we have

$$C_V dT + p dV = 0. \quad (22)$$

Inserting the ideal gas law $pV = RT$ in the above for p gives a differential expression in terms of only T and V . From this, the following sequence of manipulations (assuming constant C_V) integrates this obtaining the following

$$C_V dT + \frac{RT}{V} dV = 0 \quad (23)$$

$$\frac{dT}{T} + \frac{R}{C_V} \frac{dV}{V} = 0 \quad (24)$$

$$\log(T) + \frac{R}{C_V} \log(V) = \text{constant}. \quad (25)$$

$$TV^{\frac{R}{C_V}} = \text{constant}. \quad (26)$$

Defining $K = 1 + \frac{R}{C_V}$ the above becomes

$$TV^{K-1} = \text{constant}. \quad (27)$$

For an initial temperature, volume configuration denoted by (T_0, V_0) the above expression becomes

$$TV^{K-1} = T_0 V_0^{K-1}. \quad (28)$$

For a diatomic gas we have $K = \frac{7}{5}$, so $K - 1 = \frac{2}{5} = 0.4$. For an expansion that has its final volume V twice its initial volume size $2V_0$ we have

$$T = \frac{T_0}{2^{K-1}} = \frac{T_0}{2^{0.4}} \approx 0.75 T_0. \quad (29)$$

To derive the expression of an adiabatic expansion in terms of the variables p and V or p and T we substitute the ideal gas law in Eq. 27 as follows. From ideal gas law we have $pV = RT$ or $T = \frac{pV}{R}$ when substitute into Eq. 27 gives

$$\frac{pV}{R} V^{K-1} = \text{constant}, \quad (30)$$

or

$$pV^K = \text{constant}. \quad (31)$$

This is Fermi Eq. 39 and is the equation between the variables p and V that must be true for an adiabatic transformation of an ideal gas. In terms of p and T (replacing V with $V = \frac{RT}{p}$ in Eq. 27) it looks like

$$T \frac{(RT)^{K-1}}{p^{K-1}} = \text{constant}. \quad (32)$$

or

$$\frac{T^K}{p^{K-1}} = \text{const.} \quad (33)$$

which is equivalent to Fermi Eq. 40. Another way of obtaining the same expression can be obtained by solving for V in Eq. 27 giving

$$V = \frac{\mathcal{C}}{T^{\frac{1}{K-1}}}.$$

Here I will denote constants that don't need to be further specified by \mathcal{C} . Putting this expression for V into the ideal gas law ($pV = RT$) gives

$$\frac{p\mathcal{C}}{T^{\frac{1}{K-1}}} = RT, \quad (34)$$

or solving for p we obtain

$$p = \mathcal{C} T^{1+\frac{1}{K-1}} = \mathcal{C} T^{\frac{K}{K-1}}, \quad (35)$$

which we recognize as being equivalent to Fermi Eq. 40 again.

A Comparison of the p - V Representations of Isothermal and Adiabatic Transformations (Page 26-27)

In the (V, p) diagram $p = \frac{RT}{V} = \frac{\mathcal{C}}{V}$ for an isothermal transformation. From the previous section we see that an adiabatic transformation in the (V, p) diagram is governed by $p = \frac{\mathcal{C}}{V^K}$, with K the ratio of specific heats. To explicitly determine the slope for each of these transformations in the (V, p) plane we must evaluate the following derivatives

$$\left. \frac{dp}{dV} \right|_{\text{isotherm}} = \frac{-\mathcal{C}_1}{V^2} \quad (36)$$

and

$$\left. \frac{dp}{dV} \right|_{\text{adiabatic}} = \frac{-\mathcal{C}_2}{V^{K+1}} \quad (37)$$

We see that the adiabatic transformation will have a steeper slope when

$$\frac{-\mathcal{C}_2}{V^{K+1}} > \frac{-\mathcal{C}_1}{V^2}. \quad (38)$$

In terms of V (assuming $\mathcal{C}_1 \approx \mathcal{C}_2 > 0$ for simplicity) the above equation is equivalent to the following sequence of algebraic transformations

$$-\frac{1}{V^{K+1}} > -\frac{1}{V^2} \quad (39)$$

$$\frac{1}{V^{K+1}} < \frac{1}{V^2} \quad (40)$$

$$V^{K+1} > V^2 \quad (41)$$

$$K + 1 > 2 \quad (42)$$

$$K > 1. \quad (43)$$

Since this last equation is true for a general thermodynamical system, all previous manipulations are valid and we conclude that the slope of isothermal curve is steeper in general.

An Example of Adiabatic Expansion in the Atmosphere (Page 27)

The weight of a constant density object in a gravitational field is given by the product of the gravitational constant, the objects density, and the objects volume. For a fluid in a an infinitesimal cylindrical slab of height dh and base area A this weight is given by

$$dW = g\rho A dh .$$

To balance this weight, a pressure differential must exist between the top and bottom of the fluid (which is maintained by the internal pressure) and is given by

$$dp = \frac{dW}{A} = -\frac{g\rho A dh}{A} = -\rho g dh . \quad (44)$$

We have explicitly introduced a minus sign in the pressure differential under the expectation that the pressure should *decrease* $dp < 0$ as we move up in the atmosphere $dh > 0$. From the ideal gas law in terms of density $\rho = \frac{Mp}{RT}$ Eq. 44 can be written

$$dp = -\frac{gMp}{RT} dh \quad (45)$$

To determine the molecular weight M of air we remember that since air is about 78% Nitrogen, and 21% Oxygen so we can compute the molecular mass of air from its constitute parts

$$M_{N_2} = 2(14) = 28 \text{ g/mol} \quad (46)$$

$$M_{O_2} = 2(16) = 32 \text{ g/mol} . \quad (47)$$

So the average molecular weight of air is given by an appropriately weighted linear combination of that for Nitrogen and Oxygen

$$M_{\text{air}} = 0.78(28) + 0.21(32) \approx 28.56 \text{ g/mol} . \quad (48)$$

A more accurate calculation gives $M_{\text{air}} \approx 28.97 \text{ g/mol}$. Fermi Eq. 40 can be written as

$$Tp^{-\frac{K-1}{K}} = \mathcal{C} , \quad (49)$$

assuming the gas is expanding adiabatically. Taking the logarithm of both sides of this equation we obtain

$$\log(T) - \frac{K-1}{K} \log(p) = \log(\mathcal{C}) . \quad (50)$$

Further taking the differential of both sides of the above equation gives

$$\frac{dT}{T} - \frac{K-1}{K} \frac{dp}{p} = 0 , \quad (51)$$

or solving for $\frac{dT}{T}$ gives

$$\frac{dT}{T} = \frac{K-1}{K} \frac{dp}{p} . \quad (52)$$

Replacing the dp term with that from Eq. 45 we obtain

$$\frac{dT}{T} = - \left(\frac{K-1}{K} \right) \frac{gM}{RT} dh. \quad (53)$$

This gives for the change in temperate with respect to height the following expression

$$\frac{dT}{dh} = - \frac{K-1}{K} \frac{gM}{R}, \quad (54)$$

which is Fermi Eq. 42 in the book. Since air is mostly a diatomic gas we have that $K = \frac{7}{5}$. Taking the remaining constants to be their standard CGS values of

$$g = 980 \text{ cm/s}^2 \quad (55)$$

$$R = 8.314 \cdot 10^7 \frac{\text{dyne cm}}{\text{mol K}}, \quad (56)$$

we obtain

$$\frac{dT}{dh} = -9.8 \cdot 10^{-5} \text{ deg/cm} = -9.8 \cdot 10^{-5} \text{ deg/kilometer}. \quad (57)$$

Postulates of Reversible Thermodynamic Engines (Page 37-39)

The expression

$$L_{\text{total}} = N'L' - NL,$$

is represented in two terms, the first $N'L'$, is the work done by the first engine and the second NL is the work done by the heat. The total heat absorbed from T_2 is given by

$$Q_{2,\text{total}} = N'Q'_2 - NQ_2,$$

while the total given up to temperature T_1 , is

$$Q_{1,\text{total}} = N'Q'_1 - NQ_1.$$

With the definitions given by Fermi Eq. 47 and Fermi Eq. 48 for (L' and L) we have

$$L_{\text{total}} = N'L' - NL \quad (58)$$

$$= N'(Q'_2 - Q'_1) - N(Q_2 - Q_1) \quad (59)$$

$$= N'Q'_2 - NQ_2 - N'Q'_1 + NQ_1 \quad (60)$$

$$= Q_{2,\text{total}} - Q_{1,\text{total}}. \quad (61)$$

If $Q_{2,\text{total}} = 0$, from the above equation we have that $L_{\text{total}} = -Q_{1,\text{total}}$ which is Fermi Eq. 51.

Now as explained in the book $L_{\text{total}} \leq 0$, and because of the equivalence between the magnitude of L_{total} and $Q_{1,\text{total}}$ we therefore must have $Q_{1,\text{total}} \geq 0$. Remembering the definition

of $Q_{1,\text{total}}$ and Fermi Eq. 49 the following manipulations derive the fact that the efficiency of a *reversible* cyclic engine must be greater than that from a non-reversible cyclic engine.

$$Q_{1,\text{total}} \geq 0 \quad (62)$$

$$N'Q'_1 \geq NQ_1 \quad (63)$$

$$\frac{N'}{N}Q'_1 \geq Q_1 \quad (64)$$

$$\frac{Q_2}{Q'_2}Q'_1 \geq Q_1 \quad (65)$$

$$Q_2Q'_1 \geq Q_1Q'_2 \quad (66)$$

$$\frac{Q_2}{Q'_1} \geq \frac{Q'_2}{Q'_1} \quad (67)$$

$$\frac{Q_1}{Q_2} \leq \frac{Q'_1}{Q'_2} \quad (68)$$

$$1 - \frac{Q_1}{Q_2} \geq 1 - \frac{Q'_1}{Q'_2} \quad (69)$$

$$\eta_{\text{rev.}} \geq \eta_{\text{non-rev.}} \quad (70)$$

Carnot Cycles with an Ideal Gas (Pages 42-43)

We will step along each segment of the Carnot cycle, deriving expression that must be satisfied due to the known nature of the transformation that occurs during the considered segment. For instance, from the first law of thermodynamics we obtain that the transformation from A to B along an isothermal expansion must satisfy

$$U_B - U_A + L_{AB} = Q_{AB} \equiv Q_2. \quad (71)$$

For an isothermal expansion the work can be explicitly calculated and is found to be

$$L_{AB} = RT_2 \log\left(\frac{V_B}{V_A}\right) \quad (72)$$

Since the assumed substance is an ideal gas where the internal energy is a function of only temperature we have that $U_B = U_A$ and thus

$$Q_2 = L_{AB} = RT_2 \log\left(\frac{V_B}{V_A}\right) \quad (73)$$

Along the symmetric isothermal contraction we have

$$U_C - U_D + L_{DC} = Q_{DC} \equiv Q_1 \quad (74)$$

with (by the same reasoning $U_C = U_D$) and the above simplifies as before

$$Q_1 = L_{DC} = RT_1 \log\left(\frac{V_D}{V_C}\right) \quad (75)$$

The two paths we have not considered are the two adiabatic ones CA and BD . On the CA path the adiabatic constraint requires that

$$T_1 V_C^{K-1} = T_2 V_A^{K-1}, \quad (76)$$

and the BD path requires

$$T_2 V_B^{K-1} = T_1 V_D^{K-1}. \quad (77)$$

Dividing these two expressions gives

$$\left(\frac{V_C}{V_D}\right)^{K-1} = \left(\frac{V_A}{V_B}\right)^{K-1} \quad (78)$$

or taking the $1/(K-1)$ th root of both sides we obtain

$$\frac{V_C}{V_D} = \frac{V_A}{V_B}. \quad (79)$$

Thus in terms of Q_2 and Q_1 we have

$$\frac{Q_2}{Q_1} = \frac{RT_2 \log\left(\frac{V_B}{V_A}\right)}{RT_1 \log\left(\frac{V_D}{V_C}\right)} = \frac{T_2}{T_1}, \quad (80)$$

which expresses the ratio of heat extracted and emitted in terms of the two operating reservoir temperatures.

The Efficiency of the Carnot Cycle (Pages 43-44)

From Fermi Eq. 43 we have $L = Q_2 - Q_1$ which is equivalent to

$$1 = \frac{Q_2}{Q_1} - \frac{L}{Q_1} \quad (81)$$

Using the relationship above to express the heat ratio in terms of the reservoir temperatures we obtain

$$1 = \frac{T_2}{T_1} - \frac{L}{Q_1} \quad (82)$$

Solving for Q_1 gives

$$Q_1 = L \frac{T_1}{T_2 - T_1}, \quad (83)$$

which is Fermi Eq. 60. Now solving the above for L gives

$$L = \frac{T_1 - T_2}{T_1} Q_1 = Q_1 \left(\frac{T_2}{T_1} - 1 \right). \quad (84)$$

Proof that the Total Entropy Must Increase under Heat Flow (Page 56)

The transfer of an amount Q between bodies A_1 and A_2 results in a decrease in entropy ΔS_1 for body A_1 and an increase in entropy of ΔS_2 for body A_2 . In terms of the heat transferred at the lower temperature T_1 and the higher temperature T_2 we have

$$\Delta S_1 = \frac{Q}{T_1} \quad (85)$$

$$\Delta S_2 = -\frac{Q}{T_2}. \quad (86)$$

The total entropy change in the *entire* system is given by

$$\Delta S_1 + \Delta S_2 = \frac{Q}{T_1} - \frac{Q}{T_2} = \frac{Q(T_2 - T_1)}{T_1 T_2} > 0, \quad (87)$$

which can be seen to be positive since $T_2 > T_1$.

A Derivation of the Functional form of the Entropy (Page 58)

Since entropy is additive while probabilities are multiplicative our entropy function f must satisfy the relation $f(xy) = f(x) + f(y)$. Replaying y with $1 + \epsilon$ this becomes

$$f(x(1 + \epsilon)) = f(x) + f(1 + \epsilon). \quad (88)$$

Expanding side of the above in a Taylor series for small ϵ we obtain

$$f(x) + x\epsilon f'(x) + \frac{x^2\epsilon^2}{2}f''(x) + O(\epsilon^3) = f(x) + f(1) + f'(1)\epsilon + \frac{f''(1)}{2}\epsilon^2 + O(\epsilon^3) \quad (89)$$

or canceling the common $f(x)$ we obtain

$$x\epsilon f'(x) + O(\epsilon^2) = f(1) + f'(1)\epsilon + O(\epsilon^2). \quad (90)$$

Matching powers of epsilon on both sides we have $f(1) = 0$ and $xf'(x) = f'(1) \equiv k$ or

$$f'(x) = \frac{k}{x} \quad (91)$$

Integrating, we obtain a functional form for the entropy of $f(x) = k \log(x) + \text{constant}$.

Explicit expressions for Entropy (Pages 59-61)

The heat dQ received during an infinitesimal transformation is given by

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] dV, \quad (92)$$

which is Fermi Eq. 79. Since for a reversible transformation $dS = \frac{dQ}{T}$ the above becomes

$$dS = \frac{dQ}{T} = \frac{1}{T} \left(\frac{\partial U}{\partial T} \right)_V dT + \frac{1}{T} \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] dV \quad (93)$$

For an ideal gas the heat received during an infinitesimal transformation of an ideal gas comes in two parts as $dQ = C_V dT + p dV$ where $p = \frac{RT}{V}$, giving

$$dQ = C_V dT + \frac{RT}{V} dV \quad (94)$$

which is Fermi Eq. 84. A reversible transformation has $dS = \frac{dQ}{T}$ giving

$$dS = \frac{C_V}{T} dT + \frac{R}{V} dV. \quad (95)$$

Assuming that C_V a constant (which is true for an ideal gas) we can integrate the above to obtain

$$S = C_V \ln(T) + R \ln(V) + a. \quad (96)$$

Which is Fermi Eq. 86. Since an idea gas has $V = \frac{RT}{p}$ we can determine the entropy in terms of p and T obtaining

$$S(p, T) = C_V \ln(T) + R \ln\left(\frac{RT}{p}\right) + a. \quad (97)$$

When we expanding out the second ln term we get

$$S(p, T) = C_V \ln(T) + R \ln(R) + R \ln(T) - R \ln(p) + a \quad (98)$$

or

$$\begin{aligned} S(p, T) &= (C_V + R) \ln(T) - R \ln(p) + a + R \ln(R) \\ &= C_p \ln(T) - R \ln(p) + a + R \ln(R) \end{aligned} \quad (99)$$

which is Fermi Eq. 87. In the general case where the internal energy U is a function of *both* T and V (and C_v is not constant), then Fermi Eq. 80 requires (since S is an *exact* differential) and we can equate mixed partials

$$\frac{\partial}{\partial V} \left(\frac{1}{T} \frac{\partial U}{\partial T} \right)_V = \frac{\partial}{\partial T} \left(\frac{1}{T} \left(\left(\frac{\partial U}{\partial V} \right)_T + p \right) \right). \quad (100)$$

evaluating the derivatives of both sides we obtain

$$\frac{1}{T} \frac{\partial^2 U}{\partial V \partial T} = \left(\frac{\partial U}{\partial V} + p \right) \left(-\frac{1}{T^2} \right) + \frac{1}{T} \left(\frac{\partial^2 U}{\partial T \partial V} + \frac{\partial p}{\partial T} \right). \quad (101)$$

Which upon canceling the second derivative term from both sides gives

$$\frac{\partial U}{\partial V} + p = T \left(\frac{\partial p}{\partial T} \right)_V \quad (102)$$

or

$$\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_T - p \quad (103)$$

which is Fermi Eq. 88 in the book. Note that all the derivations up to this point have been independent of the equation of state. If in fact we further specify that our operating medium is an ideal gas with an equation of state given by the ideal gas law

$$p = \frac{RT}{V}$$

we can evaluate our general expression equation 103. For the ideal gas law this gives

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{R}{V} - \frac{RT}{V} = 0. \quad (104)$$

From which we can conclude that U does not depend on T .

Using T and p as independent variables:

Choosing (T, p) as the independent state variables Fermi Eq. 23 gives for dQ

$$dQ = \left(\left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p\right) dT + \left(\left(\frac{\partial U}{\partial p}\right)_T + p\left(\frac{\partial V}{\partial p}\right)_T\right) dp \quad (105)$$

For a reversible path we again have $dS = \frac{dQ}{T}$ (for a general path $dS \geq \frac{dQ}{T}$) and the above becomes

$$dS = \frac{1}{T} \left(\left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p\right) dT + \frac{1}{T} \left(\left(\frac{\partial U}{\partial p}\right)_T + p\left(\frac{\partial V}{\partial p}\right)_T\right) dp \quad (106)$$

Again since dS must be a perfect differential equating the cross derivatives we have

$$\frac{\partial}{\partial p} \left(\frac{1}{T} \left(\left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p\right)\right) = \frac{\partial}{\partial T} \left(\frac{1}{T} \left(\left(\frac{\partial U}{\partial p}\right)_T + p\left(\frac{\partial V}{\partial p}\right)_T\right)\right). \quad (107)$$

when we expanding the derivatives above (remembering that in this formulation p is a constant to T and vice versa) gives

$$\frac{1}{T} \left(\frac{\partial^2 U}{\partial p \partial T} + \frac{\partial V}{\partial T} + p\frac{\partial^2 V}{\partial T \partial p}\right) = \left(\left(\frac{\partial U}{\partial p}\right)_T + p\left(\frac{\partial V}{\partial p}\right)_T\right) \left(-\frac{1}{T^2}\right) \quad (108)$$

$$+ \frac{1}{T} \left(\frac{\partial^2 U}{\partial p \partial T} + p\frac{\partial^2 V}{\partial T \partial p}\right) \quad (109)$$

or when one cancels common terms, one obtains

$$\left(\frac{\partial U}{\partial p}\right)_T = -p\left(\frac{\partial V}{\partial p}\right)_T - T\left(\frac{\partial V}{\partial T}\right)_p \quad (110)$$

which is Fermi Eq. 89 in the book.

Using p and V as independent variables:

With p and V as independent variables with Fermi Eq. 24 dQ can be expressed as

$$\left(\frac{\partial U}{\partial p}\right)_V dp + \left[\left(\frac{\partial U}{\partial V}\right)_p + p\right] dV = dQ. \quad (111)$$

On a reversible path $dS = \frac{dQ}{T}$ and the above becomes

$$dS = \frac{dQ}{T} = \frac{1}{T} \left(\frac{\partial U}{\partial p}\right)_V dp + \frac{1}{T} \left[\left(\frac{\partial U}{\partial V}\right)_p + p\right] dV. \quad (112)$$

As in all previous derivations, using the knowledge that dS is a perfect differential we can equate mixed partials of S obtaining

$$\frac{\partial}{\partial V} \left(\frac{1}{T} \frac{\partial U}{\partial p}\right) = \frac{\partial}{\partial p} \left(\frac{1}{T} \left(\frac{\partial U}{\partial V} + p\right)\right) \quad (113)$$

which upon expanding the above gives us

$$\frac{\partial}{\partial V} \left(\frac{1}{T}\right) \frac{\partial U}{\partial p} + \frac{1}{T} \frac{\partial^2 U}{\partial p \partial V} = \frac{\partial}{\partial p} \left(\frac{1}{T}\right) \left(\frac{\partial U}{\partial V} + p\right) + \frac{1}{T} \left(\frac{\partial^2 U}{\partial p \partial V} + 1\right) \quad (114)$$

or

$$-\frac{1}{T^2} \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial U}{\partial p}\right)_V = -\frac{1}{T^2} \left(\frac{\partial T}{\partial V}\right)_p \left(\left(\frac{\partial U}{\partial V}\right)_p + p\right) + \frac{1}{T}. \quad (115)$$

Solving for T (by multiplying by T^2) we have

$$T = -\left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial U}{\partial p}\right)_V + \left(\frac{\partial T}{\partial p}\right)_V \left(\left(\frac{\partial U}{\partial V}\right)_p + p\right) \quad (116)$$

Which is Fermi Eq. 90. in the book.

The Derivation of the Clapeyron Equation (Page 65)

With the change in volume dV and dU given by

$$dV = (v_2(T) - v_1(T))dm \quad (117)$$

$$dU = (u_2(T) - u_1(T))dm \quad (118)$$

where v_i and u_i are the specific volume and specific internal energy of the substance. The direct ratio with

$$u_2 - u_1 + p(v_2 - v_1) = \lambda$$

gives

$$\left(\frac{dU}{dV}\right)_T = \frac{u_2(T) - u_1(T)}{v_2(T) - v_1(T)} = \frac{\lambda - p(v_2(T) - v_1(T))}{v_2(T) - v_1(T)} = \frac{\lambda}{v_2 - v_1} - p \quad (119)$$

Comparing this with equation 104 or

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_T - p \quad (120)$$

we have by inspection that

$$T \frac{dp}{dT} = \frac{\lambda}{v_2 - v_1}. \quad (121)$$

Which is Fermi Eq. 94.

An Example using the Clapeyron Equation (Page 66)

Now with the given value of λ

$$\lambda = 540 \text{ cal/gm} = 540(4.185 \cdot 10^7 \text{ erg})/\text{gm} = 2259 \cdot 10^7 \text{ erg/gm}$$

and since water boils at 100 Centigrade, $T = 100 + 273.15 = 373.15\text{K}$, so that the Clapeyron equation gives

$$\frac{dp}{dT} = \frac{(2259 \cdot 10^7 \text{ erg/gm})}{(373.15\text{K})(1677 - 1.043)\text{cm}^3/\text{gm}} = 3.61 \cdot 10^4 \text{ erg/cm}^3\text{K}$$

Remembering the conversion that

$$1 \frac{\text{dyne}}{\text{cm}^2} = 7.5 \cdot 10^{-5} \text{ cm Hg}$$

we have then

$$\frac{dp}{dT} = 2.7 \frac{\text{cm Hg}}{\text{K}}. \quad (122)$$

Normally for gas-liquid or a gas-solid interface

$$v_1 \ll v_2 \quad (123)$$

Here v_1 is the specific volume of the liquid/solid and v_2 is the specific volume of gas. Fermi Eq. 6 (the equation of state for an ideal gas) gives

$$p \frac{V}{m} = \frac{1}{M} RT. \quad (124)$$

The expression $\frac{V}{m}$ is the specific volume or the volume per gram so, since index 2 corresponds to the gas we have $v_2 = \frac{RT}{Mp}$, so that the Clapeyron equation becomes

$$\frac{dp}{dT} = \frac{\lambda}{T v_2} = \frac{\lambda}{T \left(\frac{RT}{Mp}\right)} = \frac{\lambda Mp}{RT^2} \quad (125)$$

Which is Fermi Eq. 96 in the book.

For water vapor over its liquid at the boiling temperature we get (remembering that $M = 18\text{gm/mol}$)

$$\frac{dp}{dT} = \frac{(2260 \text{ 10}^7 \text{erg/gm})(18\text{gm/mol})(1\text{atm})}{(8.314 \text{ J/molK})(373.1\text{K})^2}. \quad (126)$$

Remembering the unit conversion that $1\text{erg} = 10^{-7}\text{J}$ and $1\text{atm} = 1.01 \text{ 10}^5 \text{ Pa}$, the above becomes

$$\frac{dp}{dT} = \frac{(2260\text{J/gm})(18\text{gm/mol})(1.01 \text{ 10}^5 \text{ Pa})}{(8.314 \text{ J/molK})(373.1\text{K})^2} = 3.55 \text{ 10}^3 \text{ Pa/K} = 3.55 \text{ 10}^4 \frac{\text{dynes}}{\text{cm}^2\text{K}}. \quad (127)$$

Which agrees with the number given in the book.

In equation 125, if the heat of vaporization λ can be assumed independent of temperature then this expression can be integrated giving

$$p = C e^{\frac{\lambda M}{RT}} \quad (128)$$

As an example of a solid-liquid system consider melting of ice then we are told that

$$\lambda = 80\text{cal/cm} = 80 \times 4.185 \text{ 10}^7 \text{erg/gm} = 334.8 \text{ 10}^7 \text{erg/gm}. \quad (129)$$

so that the Clapeyron equation becomes

$$\frac{dp}{dT} = \frac{\lambda}{T(v_2 - v_1)} = \frac{335 \text{ 10}^7 \text{erg/gm}}{(273.1\text{K})(1.00013 - 1.0907)\text{cm}^3/\text{gm}} = -1.35 \text{ 10}^8 \text{erg/cm}^3\text{K} \quad (130)$$

Remembering that

$$1 \frac{\text{dyne}}{\text{cm}^2} = 9.86 \text{ 10}^{-7} \text{atm}$$

the above becomes

$$\frac{dp}{dT} = -1.33 \text{ 10}^2 \text{ atm/K} = -133 \text{ atm/K} \quad (131)$$

This increase in pressure by 134 atmospheres lowers the melting point by 1 Kelvin. The more pressure ice is under the easier it is to melt it.

The Van der Waals Critical State in terms of the constants a and b (Page 72-73)

A gas that satisfies the Van der Waal equation of state must satisfy

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT. \quad (132)$$

Given T and p , to obtain a cubic equation in V we multiply both sides of the above by V^2 and expanding the product on the left hand side producing

$$(V^2p + a)(V - b) = V^2RT \quad (133)$$

$$V^3p - bV^2p + aV - ab = V^2RT \quad (134)$$

$$pV^3 + (-bp - RT)V^2 + aV - ab = 0. \quad (135)$$

Evaluating the above at the critical pressure $p = p_c$ and temperature $T = T_c$ we have

$$p_c V^3 - (bp_c + RT_c)V^2 + aV - ab = 0. \quad (136)$$

Because the pressure and temperature are evaluated at the critical isotherm, this expression must have V_c as a root of third order. Mathematically this means that the above should be represented as $p_c(V - V_c)^3 = 0$ for some choice of V_c . Expanding this cube we have

$$p_c V^3 - 3p_c V^2 V_c + 3p_c V V_c^2 - p_c V_c^3 = 0. \quad (137)$$

Comparing these coefficients to those in Eq. 136 we have

$$-3p_c V_c = -(bp_c + RT_c) \quad (138)$$

$$3V_c^2 p_c = a \quad (139)$$

$$-p_c V_c^3 = -ab \quad (140)$$

This is a set of three equations involving three unknowns of (V_c, p_c, T_c) . Solving for V_c using the second and third equation above by dividing the third equation by the second gives

$$V_c = 3b. \quad (141)$$

Inserting this equation into the second equation from 138 we see that p_c is given by

$$p_c = \frac{a}{3V_c^2} = \frac{a}{27b^2}. \quad (142)$$

while the first equation from 138 then gives for T_c

$$T_c = \frac{3V_c p_c - bp_c}{R} = \frac{3(3b)\left(\frac{a}{27b^2}\right) - b\left(\frac{a}{27b^2}\right)}{R} = \frac{\frac{a}{b}\left(\frac{1}{3} - \frac{1}{27}\right)}{R} = \frac{8}{27} \frac{a}{Rb} \quad (143)$$

which is Fermi Eq. 100. As suggested in the text introducing the non-dimensional variables

$$\mathcal{P} = \frac{p}{p_c} \quad (144)$$

$$\mathcal{V} = \frac{V}{V_c} \quad (145)$$

$$\mathcal{T} = \frac{T}{T_c} \quad (146)$$

we get by substituting the following

$$p = \mathcal{P} p_c \quad (147)$$

$$V = \mathcal{V} V_c \quad (148)$$

$$T = \mathcal{T} T_c, \quad (149)$$

into the Van der Waals' equation of state (Fermi Eq. 99)

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT, \quad (150)$$

the following

$$\left(\mathcal{P} p_c + \frac{a}{V_c^2 \mathcal{V}^2}\right)(V_c \mathcal{V} - b) = R \mathcal{T} T_c, \quad (151)$$

or

$$\left(\mathcal{P} + \frac{a}{p_c V_c^2 \mathcal{V}^2}\right) \left(\mathcal{V} - \frac{b}{V_c}\right) = \frac{RT_c}{V_c p_c} \mathcal{J}. \quad (152)$$

Now the factors involving our recently determined critical constants simplify as follows

$$\begin{aligned} \frac{a}{p_c V_c} &= \frac{a}{\frac{a}{27b^2} 9b^2} = \frac{1}{3} = 3 \\ \frac{b}{V_c} &= \frac{b}{3b} = \frac{1}{3} \\ \frac{RT_c}{V_c p_c} &= \frac{R \left(\frac{8}{27} \frac{a}{Rb}\right)}{3b \frac{a}{27b^2}} = \frac{8}{3} \end{aligned}$$

and we get for equation 152

$$\left(\mathcal{P} + \frac{3}{\mathcal{V}^2}\right) \left(\mathcal{V} - \frac{1}{3}\right) = \frac{8}{3} \mathcal{J} \quad (153)$$

which is Fermi Eq. 101.

Expressions for internal energy and entropy in a Van der Waals gas (Page 73-75)

Using the Van der Waals equation of state expression (Fermi Eq. 99) by solving for the pressure we obtain

$$p = -\frac{a}{V^2} + \frac{RT}{V-b}. \quad (154)$$

Now for any thermodynamic system the internal energy change with respect to volume is given by (holding temperature constant)

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p. \quad (155)$$

Evaluating this expression for the $p = p(V)$ relation given by the Van der Waals equation of state we obtain

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{R}{V-b}\right) + \frac{a}{V^2} - \frac{RT}{V-b} = \frac{a}{V^2}. \quad (156)$$

Integrating this expression (with respect to V) gives

$$U = -\frac{a}{V} + f(T), \quad (157)$$

where $f(T)$ is an arbitrary function of temperature. This is Fermi Eq. 103. To derive the entropy of a Van der Waals gas we first evaluate the specific heat at constant volume given by

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = f'(T), \quad (158)$$

which if we assume that C_V is constant, we can integrate with respect to T to obtain

$$f(T) = C_V T + w.$$

This expression when put back into the expression for the internal energy U results in

$$U = -\frac{a}{V} + C_V T + w. \quad (159)$$

Now to evaluate the entropy we can perform the following manipulations exactly as in the book

$$\begin{aligned} dS &= \frac{dQ}{T} \\ &= \frac{1}{T}(dU + pdV) \\ &= \frac{1}{T}(C_V dT + \frac{a}{V^2} dV) + \frac{1}{T} \left(-\frac{a}{V^2} + \frac{RT}{V-b} \right) dV \\ &= C_V \frac{dT}{T} + \frac{a}{TV^2} dV - \frac{a}{TV^2} dV + \frac{R}{V-b} dV \\ &= C_V \frac{dT}{T} + \frac{R}{V-b} dV, \end{aligned} \quad (160)$$

which when integrated with respect to T gives

$$S = C_V \ln(T) + R \ln(V-b) + \text{constant}. \quad (161)$$

Which is Fermi Eq. 105. Compare this expression with Fermi Eq. 86 the similar expression for an ideal gas which is

$$S = C_V \ln(T) + R \ln(V) + a$$

Now along an adiabatic transformation by definition $dQ = 0$, equivalently $dS = 0$, or $S = \text{constant}$ and the above expression can be manipulated as follows

$$\begin{aligned} C_V \ln(T) + R \ln(V-b) &= C_1 \\ \ln(T) + \frac{R}{C_V} \ln(V-b) &= C_2 \\ T(V-b)^{R/C_V} &= C_3 \end{aligned} \quad (162)$$

where C_1 , C_2 , and C_3 are all constants. This expression can be recognized as Fermi Eq. 106.

The derivation of the isochore of Van't Hoff (Page 81)

The derivation given in the book proceeds smoothly until about the middle of the page where the statement $dF(A)/dT = -S(A)$ is made. This expression can be derived as follows. Considering the definition of the free energy $F(A)$ as $F = U - TS$ we have that the temperature derivative of F given by

$$\begin{aligned} \frac{dF(A)}{dT} &= \frac{dU(A)}{dT} - T \frac{dS(A)}{dT} - S(A) \\ &= \frac{1}{dT}(dU(A) - TdS(A)) - S(A) \\ &= -S(A) \end{aligned}$$

where we have used the fact that from the first and second law of thermodynamics $dU = dQ - dW = TdS - dW$ or $dU - TdS = -dW = 0$ if no work is done.

Since $S(A) = (U - F)/T$ from the definition of the free energy the temperature derivative above can be written in terms of the free energy and internal energy as

$$\frac{dF(A)}{dT} = \frac{F(A)}{T} - \frac{U(A)}{T}.$$

To relate this to the derivative of work with respect to temperature and derive the isochore of Van't Hoff recall Fermi Eq. 115 or

$$\frac{dL}{dT} = \frac{dF(A)}{dT} - \frac{dF(B)}{dT},$$

we can use the expression above to replace the derivatives of the free energy with respect to temperature with expressions involving the free energy itself as

$$\frac{dL}{dT} = \frac{dF(A)}{dT} - \frac{dF(B)}{dT} = \frac{F(A) - U(A)}{T} - \frac{F(B) - U(B)}{T}.$$

multiplying both sides by T we obtain

$$T \frac{dL}{dT} = F(A) - U(A) - (F(B) - U(B)) = F(A) - F(B) - (U(A) - U(B)) = L + \Delta U$$

where we have used Fermi Eq. 114 of $L = F(A) - F(B)$. Thus in summary we have derived

$$-\Delta U = L - T \frac{dL}{dT} \quad (163)$$

which is Fermi Eq. 117 or the isochore of Van't Hoff.

WWX: I have not finished this section ... start

WWX: page 2 of the second set of scanned notes

From Fermi Eq. 112 we have $L \leq -\Delta F$

$$pdV = \left(-\frac{\partial F}{\partial V} \right)_T \quad (164)$$

so

$$-p = \left(\frac{\partial F}{\partial V} \right)_T \quad (165)$$

Since $F = U - ST$, for an ideal gas we get that

$$F = C_v T + W - (C_v T + R \log(V) + a)T \quad (166)$$

$$= C_v T + W - T(C_p \log(T) - R \log(p) + a + R \log(R)) \quad (167)$$

Derivation of the thermodynamic potential at constant pressure (Page 82-83)

$L \leq -\Delta F$ gives $pV(B) - pV(A) \leq F(A) - F(B)$. Now defining

$$\Phi = F + pV = U - TS + pV \quad (168)$$

so that the above becomes

$$pV(B) + F(B) \leq pV(A) + F(A) \quad (169)$$

giving $\Phi(B) \leq \Phi(A)$. From the book: To find an equilibrium state for a system that has pressure and temperature we look for the minimum of the Gibbs Free energy Φ . For a general system, find what ... thermodynamic potential be it $F - U - TS$, $\Phi = U - TS + pV$ now since $\Phi = U - TS + pV$ we have that

$$\left(\frac{\partial\Phi}{\partial p}\right)_T = \left(\frac{\partial U}{\partial p}\right)_T - T\left(\frac{\partial S}{\partial p}\right)_T + V + p\left(\frac{\partial V}{\partial p}\right)_T \quad (170)$$

since $dQ = TdS = dU + pdV$,

$$T\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial U}{\partial p}\right)_T \quad (171)$$

putting this into the above we have

$$\left(\frac{\partial\Phi}{\partial p}\right)_T = \left(\frac{\partial U}{\partial p}\right)_T - \left(\frac{\partial U}{\partial p}\right)_T - p\left(\frac{\partial V}{\partial p}\right)_T + V + p\left(\frac{\partial V}{\partial p}\right)_T = V \quad (172)$$

which is Fermi Eq. 123. In the same way

$$\left(\frac{\partial\Phi}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p - S - T\left(\frac{\partial S}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p \quad (173)$$

$$TdS = dU + pdV \quad (174)$$

so that

$$T\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p \quad (175)$$

when put in the above becomes

$$\left(\frac{\partial\Phi}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p - S - \left(\frac{\partial U}{\partial T}\right)_p - p\left(\frac{\partial V}{\partial T}\right)_p + \left(p\frac{\partial V}{\partial T}\right)_p \quad (176)$$

$\Phi = U - TS + pV$. Now T is the same for both vapor and liquid phases and P is the same for both vapor and the liquid at least at the surface or in zero gravity? Now $\Phi = \Phi_1 + \Phi_2$, i.e. on the space shuttle or with very little liquid. $pV = RT$ and

$$\Phi = m_1\phi_1(T) + m_2\phi_2(T) \quad (177)$$

Let $m_1 \rightarrow m_1 + dm$, then Φ becomes

$$\Phi' = (m_1 + dm_1)\phi_1(T) + (m_2 - dm_1)\phi_2(T) = \Phi + dm_1(\phi_1 - \phi_2) \quad (178)$$

As Φ was at a minimum. In order that the value of Φ' not change from that of Φ , we must have $\phi_1 = \phi_2$, which is

$$U_1 - TS_1 + pV_1 = U_2 - TS_2 + pV_2 \quad (179)$$

or

$$U_2 - U_1 - T(S_2 - S_1) + p(V_2 - V_1) = 0 \quad (180)$$

taking the partial with respect to T we have

$$\frac{d}{dT}(U_2 - U_1) - (S_2 - S_1) - T \frac{d}{dT}(S_2 - S_1) + \frac{dp}{dT}(V_2 - V_1) + p \frac{d}{dT}(V_2 - V_1) = 0 \quad (181)$$

$$T \frac{ds}{dT} = \frac{dU}{dT} + p \frac{dv}{dT} \quad (182)$$

$$\frac{dU}{dT} - T \frac{dS}{dT} + p \frac{dV}{dT} = 0 \quad (183)$$

$$-(S_2 - S_1) + \frac{dp}{dT}(V_2 - V_1) = 0 \quad (184)$$

with $S_2 - S_1 = \frac{\lambda}{T}$, we obtain

$$\frac{dp}{dT} = \frac{\lambda}{T(V_2 - V_1)} \quad (185)$$

$$\Phi = U - TS + pV \quad (186)$$

$$= c_V T + W - T(C_p \log(T) - R \log(p) + a + R \log(R)) + pV \quad (187)$$

$$= c_V T + W + pV - T(C_p \log(T) - R \log(p) + a + R \log(R)) \quad (188)$$

$$= c_V T + W + RT - T(C_p \log(T) - R \log(p) + a + R \log(R)) \quad (189)$$

since $C_V + R = C_p$ the above becomes

$$\Phi = C_p T + W - T(C_p \log(T) - R \log(p) + a + R \log(R)) \quad (190)$$

$$\frac{dF(A)}{dT} = \frac{dU}{dT} - T \frac{dS}{dT} - S(A) \quad (191)$$

$$= \frac{1}{dT}(dU - TdS) - S(A) \quad (192)$$

$$= -S(A) \quad (193)$$

if no work is done? Since

$$dU = dQ - dW = TdS - dW \quad (194)$$

so we have that $dU - TdS = -dW = 0$ if there is no work done.

$$\frac{dF(A)}{dT} = \frac{F(A)}{T} - \frac{U(A)}{T} \quad (195)$$

since $F = U - ST$, we have that $-S = \frac{F-U}{T}$, now Fermi Eq. 114 is that $L = F(A) - F(B)$ and

$$\frac{dL}{dT} = \frac{dF(A)}{dT} - \frac{dF(B)}{dT} \quad (196)$$

then

$$T \frac{dL}{dT} = T \frac{dF(A)}{dT} - T \frac{dF(B)}{dT} \quad (197)$$

each term in the above can be replaced as

$$T \frac{dL}{dT} = F(A) - U(A) - (F(B) - U(B)) = F(A) - F(B) - (U(A) - U(B)) = L + \Delta U \quad (198)$$

so we have

$$T \frac{dL}{dT} = L + \Delta U \quad (199)$$

giving

$$-\Delta U = L - T \frac{dL}{dT} \quad (200)$$

which is Fermi Eq. 117. From Fermi Eq. 112 we have $L \leq -\Delta F$

$$pdV = - \left. \frac{\partial F}{\partial V} \right|_T \quad (201)$$

so

$$-p = \left(\frac{\partial F}{\partial V} \right)_T \quad (202)$$

Since $F = U - ST$, for an ideal gas we get that

$$F = C_v T + W - (C_v T + R \log(V) + a)T \quad (203)$$

$$= C_v T + W - T(C_p \log(T) - R \log(p) + a + R \log(R)) \quad (204)$$

$L \leq -\Delta F$ gives $pV(B) - pV(A) \leq F(A) - F(B)$. Now defining

$$\Phi = F + pV = U - TS + pV \quad (205)$$

so that the above becomes

$$pV(B) + F(B) \leq pV(A) + F(A) \quad (206)$$

giving $\Phi(B) \leq \Phi(A)$. From the book: To find an equilibrium state for a system that has pressure and temperature we look for the minimum of the Gibbs Free energy Φ . For a general system, find what ... thermodynamic potential be it $F - U - TS$, $\Phi = U - TS + pV$ now since $\Phi = U - TS + pV$ we have that

$$\left(\frac{\partial \Phi}{\partial p} \right)_T = \left(\frac{\partial U}{\partial p} \right)_T - T \left(\frac{\partial S}{\partial p} \right)_T + V + p \left(\frac{\partial V}{\partial p} \right)_T \quad (207)$$

since $dQ = TdS = dU + pdV$,

$$T \left(\frac{\partial S}{\partial p} \right)_T = \left(\frac{\partial U}{\partial p} \right)_T \quad (208)$$

putting this into the above we have

$$\left. \frac{\partial \Phi}{\partial p} \right|_T = \left. \frac{\partial U}{\partial p} \right|_T - \left. \frac{\partial U}{\partial p} \right|_T - p \left. \frac{\partial V}{\partial p} \right|_T + V + p \left. \frac{\partial V}{\partial p} \right|_T = V \quad (209)$$

which is Fermi Eq. 123. In the same way

$$\left. \frac{\partial \Phi}{\partial T} \right|_p = \left. \frac{\partial U}{\partial T} \right|_p - S - T \left. \frac{\partial S}{\partial T} \right|_p + p \left. \frac{\partial V}{\partial T} \right|_p \quad (210)$$

$$TdS = dU + pdV \quad (211)$$

so that

$$T \left. \frac{\partial S}{\partial T} \right|_p = \left. \frac{\partial U}{\partial T} \right|_T + p \left. \frac{\partial V}{\partial T} \right|_p \quad (212)$$

when put in the above becomes

$$\left. \frac{\partial \Phi}{\partial T} \right|_p = \left. \frac{\partial U}{\partial T} \right|_p - S - \left. \frac{\partial U}{\partial T} \right|_p - p \left. \frac{\partial V}{\partial T} \right|_p + p \left. \frac{\partial V}{\partial T} \right|_p \quad (213)$$

$\Phi = U - TS + pV$. Now T is the same for both vapor and liquid phases and P is the same for both vapor and the liquid at least at the surface or in zero gravity? Now $\Phi = \Phi_1 + \Phi_2$, i.e. on the space shuttle or with very little liquid. $pV = RT$ and

$$\Phi = m_1 \phi_1(T) + m_2 \phi_2(T) \quad (214)$$

Let $m_1 \rightarrow m_1 + dm$, then Φ becomes

$$\Phi' = (m_1 + dm_1) \phi_1(T) + (m_2 - dm_1) \phi_2(T) = \Phi + dm_1 (\phi_1 - \phi_2) \quad (215)$$

As Φ was at a minimum. In order that the value of Φ' not change from that of Φ , we must have $\phi_1 = \phi_2$, which is

$$U_1 - TS_1 + pV_1 = U_2 - TS_2 + pV_2 \quad (216)$$

or

$$U_2 - U_1 - T(S_2 - S_1) + p(V_2 - V_1) = 0 \quad (217)$$

taking the partial with respect to T we have

$$\frac{d}{dT}(U_2 - U_1) - (S_2 - S_1) - T \frac{d}{dT}(S_2 - S_1) + \frac{dp}{dT}(V_2 - V_1) + p \frac{d}{dT}(V_2 - V_1) = 0 \quad (218)$$

$$T \frac{ds}{dT} = \frac{dU}{dT} + p \frac{dv}{dT} \quad (219)$$

$$\frac{dU}{dT} - T \frac{dS}{dT} + p \frac{dV}{dT} = 0 \quad (220)$$

$$-(S_2 - S_1) + \frac{dp}{dT}(V_2 - V_1) = 0 \quad (221)$$

with $S_2 - S_1 = \frac{\lambda}{T}$, we obtain

$$\frac{dp}{dT} = \frac{\lambda}{T(V_2 - V_1)} \quad (222)$$

$$\Phi = U - TS + pV \quad (223)$$

$$= c_V T + W - T(C_p \log(T) - R \log(p) + a + R \log(R)) + pV \quad (224)$$

$$= c_V T + W + pV - T(C_p \log(T) - R \log(p) + a + R \log(R)) \quad (225)$$

$$= c_V T + W + RT - T(C_p \log(T) - R \log(p) + a + R \log(R)) \quad (226)$$

since $C_V + R = C_p$ the above becomes

$$\Phi = C_p T + W - T(C_p \log(T) - R \log(p) + a + R \log(R)) \quad (227)$$

$$\Phi_i = \Phi_i(T, p, m_{i,1}, m_{i,2}, m_{i,3}, \dots, m_{i,n}) \quad (228)$$

$$\Phi_i(T, p, km_{i,1}, km_{i,2}, km_{i,3}, \dots, km_{i,n}) = k\Phi_i(T, p, m_{i,1}, m_{i,2}, \dots, m_{i,n}) \quad (229)$$

which is homogeneous of degree 1.

$$\dot{k} = m_{i,k} - \delta m \quad (230)$$

$$m_{j,k'} = m_{j,k} + \delta m \quad (231)$$

$$\delta\Phi = \delta\Phi_i + \delta\Phi_j \quad (232)$$

$$= \frac{\partial\Phi_i}{\partial m_{i,k}}(-\delta m) + \frac{\partial\Phi_j}{\partial m_{j,k}}\delta m \quad (233)$$

$$= \frac{\partial\Phi_j}{\partial m_{j,k}}\delta m - \frac{\partial\Phi_i}{\partial m_{i,k}}\delta m = 0 \quad (234)$$

$$\frac{\partial\Phi_j}{\partial m_{j,k}} = \frac{\partial\Phi_i}{\partial m_{i,k}} \quad (235)$$

How many equations like this do we have? f phases and n components, since each component n of them in a given phase i can go to any of the other $f - 1$ phase (nothing happens if it goes to itself. We have $n(f - 1)$ equations for equilibrium. Each $\frac{\partial\Phi}{\partial}$ depends only on ratios of the $m_{k,i}$. The number of ratios there are like this are $n - 1$. Then for all $\frac{\partial\Phi_i}{\partial}$ is $f(n - 1)$ with T and p we have $f(n - 1) + 2$ variables. Let v be the number of unknowns minus the number of equation. Then

$$v = (n - 1)f + 2 - n(f - 1) \quad (236)$$

$$= 2 + n - f \quad (237)$$

which is Fermi Eq. 131. Now example #1 we have

$$v = 2 + 1 - 1 = 2 \quad (238)$$

Now example #2 we have

$$v = 2 + 2 - 1 = 3 \quad (239)$$

Now example #3 is 2 phases solid and liquid has $f = 2$ and one component so $n = 1$ so we have

$$v = 2 + n - f = 2 + 1 - 2 = 1 \quad (240)$$

Now in example #4 we have $n = 1$ and $f = 3$ so we have

$$v = 2 + n - f = 2 + 1 - 3 = 0 \quad (241)$$

we have $L = ev$. Power exerted by DC current is given by $P = VI$ with V the voltage and I the current. Now current is charge per unit time. Thus the work is voltage times charge.

$$U(T, e) = U(T) - eU(T) \quad (242)$$

$$\Delta U = -eU(T) \quad (243)$$

isochore of Vanft Hoff

$$L - T \frac{dL}{dT} = -\Delta U \quad (244)$$

$$eV - T \frac{d(eV)}{dT} = eU \quad (245)$$

$$v - T \frac{dv}{dT} = u \quad (246)$$

which is Fermi Eq. 134. $e = Cv(T)$ and $dL = \frac{1}{2}dCV^2(T)$ energy of an isolated capacitor is given by

$$\frac{1}{2} \frac{e^2}{C} \quad (247)$$

$$dL = -d\left(\frac{1}{2} \frac{e^2}{C}\right) = \frac{1}{2} \frac{e^2}{C^2} dC \quad (248)$$

But $e = Cv$ and $dL = \frac{1}{2} \frac{C^2 v^2}{C^2} dC = \frac{1}{2} v^2 dC$

$$U(T, e) = U(T) - eu(T) = U(T) - Cv(T)u(T) \quad (249)$$

plus energy now present in condenser, heat released/absorbed when

$$dQ = dU + dL = d(U(T) - Cv(T)u(T) + \frac{1}{2}Cv^2(T)) + \frac{1}{2}dCv^2 \quad (250)$$

$$= dT \left(\frac{dU}{dT} - C \frac{dv}{dT} u - Cv \frac{dU}{dT} + Cv \frac{dv}{dT} \right) \quad (251)$$

$$+ dC \left(-vu + \frac{1}{2}v^2 + \frac{1}{2}v^2 \right) \quad (252)$$

$$dS = \frac{dQ}{T} = \frac{dT}{T} \left(\frac{dU}{dT} - Cv \frac{du}{dT} - Cu \frac{dv}{dT} + Cv \frac{dv}{dT} \right) \quad (253)$$

$$+ \frac{dC}{T} (v^2 - vu) \quad (254)$$

$$\frac{\partial}{\partial C} \left[\frac{\frac{dU}{dT} - Cv \frac{dU}{dT} - Cu \frac{dv}{dT} + Cv \frac{dV}{dT}}{T} \right] = \frac{\partial}{\partial T} \left[\frac{v^2 - vu}{T} \right] \quad (255)$$

$$\frac{1}{T} \left(-v \frac{dU}{dT} - u \frac{dV}{dT} + v \frac{dv}{dT} \right) \quad (256)$$

$$= -\frac{v^2 - vu}{T^2} + \frac{2vv' - v'u - vu'}{T} \quad (257)$$

which gives

$$-\frac{v}{T} \frac{du}{dT} - \frac{u}{T} \frac{dv}{dT} + \frac{v}{T} \frac{dv}{dT} = \frac{2v}{T} \frac{dv}{dT} - \frac{u}{T} \frac{dv}{dT} - \frac{v}{T} \frac{du}{dT} - \frac{v^2}{T^2} + \frac{vu}{T^2} \quad (258)$$

$$\frac{v^2}{T^2} - \frac{vu}{T^2} = \frac{v}{T} \frac{dv}{dT} \quad (259)$$

$$\frac{v}{T} - \frac{u}{T} = \frac{dv}{dT} \quad (260)$$

which gives

$$v - T \frac{dv}{dT} = u \quad (261)$$

which is Fermi Eq. 134.

End page 10 of second set of scanned notes

begin page 13 of second set of scanned notes

In Fermi Eq. 136 if $k(T) \ll 1$ then

$$[A_1]^{n_1} [A_2]^{n_2} \dots [A_r]^{n_r} = k(T) [\beta_1]^{m_1} [\beta_2]^{m_2} \dots [\beta_s]^{m_s} \quad (262)$$

Generally we have that $[A_1]^{n_1} [A_2]^{n_2} \dots [A_r]^{n_r} \ll 1$, so the reaction is shifted to the right. Now the definition of $[A]$ is the number of moles of A divided by the volume. So $[A]M$ is the mass of A divided by the volume.

$$L_I = -RT \sum_{i=1}^n n_i \quad (263)$$

$$p_1 V_1 = n_1 RT \quad (264)$$

since $p \propto \frac{n}{V} RT$ we have that $p \propto [H] RT$, so the pressure is proportional to the mole concentration. To insure that we get m_1 moles in the first cylinder which we can extend to $+\infty$ we must require that

$$V_1 [\beta_1] = m_1 \quad \Rightarrow \quad V_1 = \frac{m_1}{[\beta_1]} \quad (265)$$

where $[\beta_1]$ concentration of elements β_1 .

$$L = L_I + L_{II} \quad (266)$$

$$= RT \left(\sum_{j=1}^s m_j - \sum_{i=1}^n n_i \right) = -\Delta F \quad (267)$$

as this process is isothermal and reversible. We have that

$$F_1 = n_1 \{ C_{v_1} T + w_1 - T(C_{v_1} \log(T) + R \log(\frac{1}{[A]}) + a_1) \} \quad (268)$$

$$= n_1 \{ C_{v_1} T + w_1 - T(C_{v_1} \log(T) - R \log([A]) + a_1) \} \quad (269)$$

$$(270)$$

The Free energy initially is given by

$$F_I = \sum_{i=1}^r n_i \{C_{v_i} T + w_i - T(C_{v_i} \log(T) - R \log([A_i]) + a_i)\} \quad (271)$$

$$F_F = \sum_{j=1}^s m_j \{C'_{v_j} T + w'_j - T(C'_{v_j} \log(T) - R \log([B_j]) + a'_j)\} \quad (272)$$

$F_I - F_F = L$ becomes

$$RT \left(\sum_{j=1}^s m_j - \sum_{i=1}^r n_i \right) = \sum_{i=1}^r n_i \{C_{v_i} T + w_i - T(C_{v_i} \log(T) - R \log([A_i]) + a_i)\} - \sum_{j=1}^s m_j \{C_{v_i} T + w_i - T(C_{v_i} \log(T) - R \log([A_i]) + a_i)\} \quad (273)$$

so we have then that

$$RT \left(\sum_{j=1}^s m_j - \sum_{i=1}^r n_i \right) = \sum_{i=1}^r n_i C_{v_i} T + n_i w_i - n_i T C_{v_i} \log(T) + n_i R T \log([A_i]) + n_i a_i T - \sum_{j=1}^s m_j C'_{v_j} T + m_j w'_j - m_j T C'_{v_j} \log(T) + m_j R T \log([B_j]) + m_j a'_j T \quad (274)$$

dividing by RT we have

$$\sum_{j=1}^s m_j - \sum_{i=1}^r n_i = \sum_{i=1}^r \frac{n_i C_{v_i}}{R} + \frac{n_i w_i}{RT} - \frac{n_i C_{v_i} \log(T)}{R} + n_i \log([A_i]) + \frac{n_i a_i}{R} \quad (275)$$

$$+ \sum_{j=1}^s \frac{m_j C'_{v_j}}{R} + \frac{m_j w'_j}{RT} - \frac{m_j C'_{v_j} \log(T)}{R} + m_j \log([B_j]) + \frac{m_j a'_j}{R} \quad (276)$$

so we have that

$$\sum_{i=1}^r n_i \log([A_i]) - \sum_{j=1}^s m_j \log([B_j]) = - \sum_{i=1}^r \frac{n_i C_{v_i}}{RT} + \frac{n_i w_i}{RT} - \frac{n_i C_{v_i} \log(T)}{R} + \frac{n_i a_i}{R} + n_i \quad (277)$$

$$+ \sum_{j=1}^s \frac{m_j C'_{v_j}}{R} + \frac{m_j w'_j}{RT} - \frac{m_j C'_{v_j} \log(T)}{R} + \frac{m_j a'_j}{R} + m_j \quad (278)$$

which gives

$$\log \left(\frac{[A_1]^{n_1} [A_2]^{n_2} \dots [A_r]^{n_r}}{[B_1]^{m_1} [B_2]^{m_2} \dots [B_s]^{m_s}} \right) = \sum_{i=1}^r \frac{n_i C_{v_i} \log(T)}{R} - \sum_{j=1}^s \frac{m_j C'_{v_j} \log(T)}{R} \quad (279)$$

$$+ - \sum_{i=1}^r \frac{n_i w_i}{RT} + \sum_{j=1}^s \frac{m_j w'_j}{RT} \quad (280)$$

$$+ - \sum_{i=1}^r \frac{n_i C_{v_i}}{RT} + \frac{n_i a_i}{R} + n_i \quad (281)$$

$$\sum_{j=1}^s \frac{m_j C'_{v_j}}{RT} + \frac{m_j a'_j}{R} + m_j \quad (282)$$

Therefore we have that

$$\log(\dots) = \log\left(\frac{T^{\frac{n_1 C_{v1}}{R}} T^{\frac{n_2 C_{v2}}{R}} T^{\frac{n_3 C_{v3}}{R}} \dots T^{\frac{n_r C_{vr}}{R}}}{T^{\frac{m_1 C_{v1}}{R}} T^{\frac{m_2 C_{v2}}{R}} T^{\frac{m_3 C_{v3}}{R}} \dots T^{\frac{m_s C_{vs}}{R}}}\right) - \sum_{i=1}^r \log(\exp(\frac{n_i w_i}{RT})) + \sum_{j=1}^s \log(\exp(\frac{m_j w'_j}{RT})) \quad (283)$$

$$- \sum_{i=1}^r \log(\exp(\frac{n_i C_{v_i}}{R} + \frac{n_i a_i}{R} + n_i)) + \sum_{j=1}^s \log(\exp(\frac{m_j C'_{v_j}}{R} + \frac{m_j a'_j}{R} + m_j)) \quad (284)$$

or

$$\log(\dots) = \log(T^{\frac{1}{R} \sum_{i=1}^r n_i C_{v_i} - \frac{1}{R} \sum_{j=1}^s m_j C'_{v_j}}) + \log\left(\frac{\exp(\sum_{j=1}^s \frac{m_j w'_j}{RT})}{\exp(\sum_{i=1}^r \frac{n_i w_i}{RT})}\right) + \log\left(\frac{\exp(\sum_{j=1}^s \frac{m_j C'_{v_j}}{R} + \frac{m_j a'_j}{R} + m_j)}{\exp(\sum_{i=1}^r \frac{n_i C_{v_i}}{R} + \frac{n_i a_i}{R} + n_i)}\right) \quad (285)$$

Taking exponentials we have

$$\frac{[A_1]^{n_1} [A_2]^{n_2} \dots [A_r]^{n_r}}{[B_1]^{m_1} [B_2]^{m_2} \dots [B_s]^{m_s}} = \exp\left(\frac{1}{R} \left\{ \sum_{j=1}^s m_j (R' + C'_{v_j} + a_j) - \sum_{i=1}^r n_i (R + C_{v_i} + a_i) \right\}\right) \quad (286)$$

which is times

$$T^{\frac{1}{R} (\sum_{i=1}^r n_i C_{v_i} - \sum_{j=1}^s m_j C'_{v_j})} \quad (287)$$

which is times the following

$$\exp\left(-\frac{1}{RT} \left(\sum_{i=1}^r n_i w_i - \sum_{j=1}^s m_j w'_j \right)\right) \quad (288)$$

which gives Fermi Eq. 139. This gives $p_i V = n_i R T$, so $p_i = \frac{n_i R T}{V}$ with $p = \sum_i p_i = \frac{R T}{V} \sum_i n_i$. Since $F = U - T S$ and $\Phi = U - T S + p V$ the Free energy is given by

$$C_{v1} T + W_1 - T(C_{v1} \log(T) - R \log([A_1]) + a_1) + V[A_1](C_{v1} T + W_1 - T(C_{v1} \log(T) - R \log([A_1]) + a_1)) \quad (289)$$

so

$$F = V \sum_{i=1}^r [A_i](C_{v_i} T + W_i - T(C_{v_i} \log(T) - R \log([A_i]) + a_i)) + V \sum_{j=1}^s [B_j](C'_{v_j} T + W'_j - T(C'_{v_j} \log(T) - R \log([B_j]))) \quad (290)$$

Which is Fermi Eq. 140. Thus the variation on F is given by

$$\delta F = -\frac{\partial F}{\partial [A_1]} \epsilon n_1 - \frac{\partial F}{\partial [A_2]} \epsilon n_2 - \frac{\partial F}{\partial [A_3]} \epsilon n_3 - \dots - \frac{\partial F}{\partial [A_r]} \epsilon n_r + \frac{\partial F}{\partial [B_1]} \epsilon m_1 + \frac{\partial F}{\partial [B_2]} \epsilon m_2 + \frac{\partial F}{\partial [B_3]} \epsilon m_3 + \dots + \frac{\partial F}{\partial [B_s]} \epsilon m_s \quad (291)$$

which gives

$$-\frac{\partial F}{\partial [A_1]} [A_1] - \frac{\partial F}{\partial [A_2]} [A_2] - \frac{\partial F}{\partial [A_3]} [A_3] - \dots - \frac{\partial F}{\partial [A_r]} [A_r] + \frac{\partial F}{\partial [B_1]} [B_1] + \frac{\partial F}{\partial [B_2]} [B_2] + \frac{\partial F}{\partial [B_3]} [B_3] + \dots + \frac{\partial F}{\partial [B_s]} [B_s] = 0 \quad (292)$$

From Fermi Eq. 140. we have

$$\frac{\partial F}{\partial [A_i]} = V \sum_{i=1}^r (C_{v_i} + W_i - T(C_{v_i} \log(T) - R \log([A_i]) + a_i) + V \sum_{i=1}^r [A_i] \frac{TR}{[A_i]} = V T R \quad (293)$$

This is incorrect. You are taking the derivative of the concentration $[A_i]$ not the summation variable $[A_i]$. The above is taking the derivative of the summation variable index $[A_i]$ we get

$$\frac{\partial F}{\partial [A_i]} = V \{C_{v_i}T + w_i - T(C_{v_i} \log(T) - R \log([A_i]) + a_i)\} + V[A_i] \frac{RT}{[A_i]} = V \{C_{v_i}T + w_i - T(C_{v_i} \log(T) - R \log([A_i]) + a_i) + RT\} \quad (294)$$

In the same way

$$\frac{\partial F}{\partial [B_i]} \quad (295)$$

Then

$$\delta F = -[A_1]V(C_{v_1}T + w_1 - T(C_{v_1} \log(T) - R \log([A_1]) + a_1) + RT) - [A_2]V(C_{v_2}T + w_2 - T(C_{v_2} \log(T) - R \log([A_2]) + a_2) + RT) \quad (296)$$

or

$$- \sum_{i=1}^r n_i \{C_{v_i}T + w_i - T(C_{v_i} \log(T) - R \log([A_i]) + a_i) + RT\} + \sum_{j=1}^s m_j \{C'_{v_j}T + w'_j - T(C'_{v_j} \log(T) - R \log([B_j]) + b_j) + RT\} \quad (297)$$

$$\Delta U = \sum_{j=1}^s m_j (C'_{v_j}T + w'_j) - \sum_{i=1}^r n_i (C_{v_i}T + w_i) \quad (298)$$

$$H = -\Delta U = \sum_{i=1}^r n_i (C_{v_i}T + w_i) - \sum_{j=1}^s m_j (C'_{v_j}T + w'_j) \quad (299)$$

$$\frac{d \log(k(T))}{dT} = \frac{1}{TR} \left(\sum_{i=1}^r C_{v_i} n_i - \sum_{j=1}^s C'_{v_j} m_j \right) + \frac{1}{RT^2} \quad (300)$$

To exclude the logarithm derivative of 141 write

$$k(T) = C_1 T^{C_2} e^{-\frac{C_3}{RT}} \quad (301)$$

so that

$$\log(k(T)) = \log(C_1) + C_2 \log(T) - \frac{C_3}{RT} \log(e) = \log(C_1) + C_2 \log(T) - \frac{C_3}{RT} \quad (302)$$

so that

$$\begin{aligned} \frac{d \log(k(T))}{dT} &= \frac{C_2}{T} + \frac{C_3}{RT^2} \\ \frac{1}{RT} \left(\sum_{i=1}^r C_{v_i} n_i - \sum_{j=1}^s C'_{v_j} m_j \right) + \frac{1}{RT^2} \left(\sum_{i=1}^r n_i w_i - \sum_{j=1}^s m_j w'_j \right) &= \frac{1}{RT^2} \left(\sum_{i=1}^r T C_{v_i} n_i + n_i w_i - \sum_{j=1}^s T C'_{v_j} m_j - m_j w'_j \right) \\ &= \frac{H}{RT^2} \end{aligned}$$

Note that $H = H(T)$ thus we can see the temperature dependence. If $n_1 + n_2 + \dots + n_r < m_1 + m_2 + \dots + m_s$, then shifting the equation to the right increases the pressure.

$$\frac{[A_1]^{n_1}[A_2]^{n_2} \dots [A_r]^{n_r}}{[B_1]^{n_1}[B_2]^{n_2} \dots [B_s]^{n_s}} = k(T) \quad (307)$$

Compress the system shrinking V causes the concentrations $[A]$ and $[B]$ to increase. Because of the concentration inequality $n_1 + n_2 + \dots + n_r < m_1 + m_2 + \dots + m_s$ the left hand side decreases to prevent this $[A]$ increases by the $[B]$ stays the same which implies that the reaction shifts towards the reactants.

Problem 1

$2A \rightarrow A$ which gives

$$\frac{[A]^2}{[A_2]} = k(T) \quad (308)$$

is the equation of the law of mass action. Here $[A]$ is in units of number of moles per the volume and we are told that our reaction constant k is given by $k(18C) = 1.7 \cdot 10^{-4}$. Dalton's law of partial pressure says that $p = 1 \text{ atm} = p_A + p_{A_2}$ with p_A the partial pressure of the A species and p_{A_2} the partial pressure of the A_2 species. Then we have that

$$p_A = \frac{n_A RT}{V} = [A]RT \quad (309)$$

and

$$p_{A_2} = [A_2]RT \quad (310)$$

so

$$p = ([A] + [A_2])RT \quad (311)$$

so $[A]^2 = k(T)[A_2]$ which when put in above we have

$$p = ([A] + \frac{[A]^2}{k(T)})RT \quad (312)$$

or

$$\frac{[A]^2}{k(T)} + [A] - \frac{p}{RT} = 0 \quad (313)$$

which is a quadratic equation for $[A]$. Since

$$\frac{p}{RT} = \frac{1.01 \cdot 10^5 \text{ Pa}}{(8.314 \text{ J/molK})(273.15 + 18 \text{ K})} = \frac{41.72 \text{ J/mol}^3}{\text{J/mol}} = 41.72 \text{ mol/m}^3 \quad (314)$$

so we have for $[A]$ the following

$$[A] = \frac{-1 \pm \sqrt{1 - 4 \frac{1}{k(T)} \left(\frac{-p}{RT}\right)}}{2 \left(\frac{1}{k(T)}\right)} = \frac{-1 \pm \sqrt{1 + \frac{4p}{k(T)RT}}}{\frac{2}{k(T)}} = 8.413 \cdot 10^{-2} \text{ mol/V} \quad (315)$$

so the concentration of $[A_2]$

$$[A_2] = \frac{RT}{p} - [A] = 41.72 - 8.413 \cdot 10^{-2} = 41.64 \text{ mol/m}^3 \quad (316)$$

we can check this by considering

$$\frac{[A]^2}{[A_2]} = 1.6997 \cdot 10^{-4} \quad (317)$$

since we are asked for the percentage of A we remember that $n_A = [A]V$ and $n_{A_2} = [A_2]V$ so the percentage of A is given by $= \frac{n_A}{n_A + n_{A_2}} = \frac{[A]V}{[A]V + [A_2]V} = \frac{[A]}{[A] + [A_2]} = 2.01 \cdot 10^{-3} = 0.201$

Problem 2

We have $H = 50000 \text{ cal/mol}$ degree of dissociation a $H > 0$ which means that this is an exothermal reaction expect raising the temperature to shift the reaction towards the left and we should have an increase in the concentration of A . If I write the equation for the chemical reaction in the other order, I would flip the concentration ratio $\frac{[A]^2}{[A_2]}$ but would not change the term $e^{-H/RT}$ which would give a different equation. Where is the inconsistency. Would be then than H should be given as the heat of reaction from the left to right. Which if we switch the order of the chemical equation we switch the *sign* of H .

$$\frac{d \log(k(T))}{dT} = \frac{H}{RT^2} \quad (318)$$

so

$$\log(k(T)) = C_1 - \frac{H}{RT} \quad (319)$$

so that

$$k(T) = C_2 e^{-\frac{H}{RT}} \quad (320)$$

therefore we have

$$\frac{[A]^2}{[A_2]} = C_2 e^{-\frac{H}{RT}} = k(T) \quad (321)$$

What is C_2 ? We know that $k(T = 18 \text{ C} = 291.15) = 1.7 \cdot 10^{-4}$ so that

$$RT = (8.314 \text{ J/molK})(291.15 \text{ K}) = 2.42 \cdot 10^3 \text{ J/mol}$$

since we know that $1 \text{ J} = 0.2388 \text{ cal}$ we have that $RT = 5.78 \cdot 10^3 \text{ cal/mol}$, so that

$$\frac{H}{RT} = \frac{50000 \text{ cal/mol}}{5.78 \cdot 10^3 \text{ cal/mol}} = 8.64 \cdot 10^1 \quad (322)$$

$$C_2 \exp(-8.64 \cdot 10^1) = 1.7 \cdot 10^{-4} \quad (323)$$

which gives $C_2 = \exp(8.64 \cdot 10^1) \cdot 1.7 \cdot 10^{-4} = 5.66 \cdot 10^{33}$, which is huge. Therefore $k(T = 18 \text{ C}) = 5.66 \cdot 10^{33} \exp(-\frac{H}{RT}) = 2.07 \cdot 10^{-4}$. Now to find the percentage of A we remember that $p = p_A + p_{A_2} = [A]RT + [A_2]RT$

$$[A] + [A_2] = \frac{P}{RT} \quad \text{and} \quad [A]^2 = k(T)[A_2] \quad (324)$$

$$[A] + \frac{[A]^2}{k(T)} = \frac{p}{RT} \Rightarrow \frac{[A]^2}{k(T)} + [A] - \frac{p}{RT} = 0 \quad (325)$$

solving for $[A]$ we have

$$[A] = \frac{-1 \pm \sqrt{1 - 4 \left(\frac{1}{k(T)}\right) \left(\frac{-P}{RT}\right)}}{2 \left(\frac{1}{k(T)}\right)} = 9.26 \cdot 10^{-2} > 8.41 \cdot 10^{-2} \quad (326)$$

so the concentration of species A_2 is given by

$$[A_2] = \frac{[A]^2}{k(T)} \Rightarrow [A_2] = 4.14 \cdot 10^1 < 4.16 \cdot 10^1 \quad (327)$$

so the percentage A is given by $2.22 \cdot 10^{-3}$ or 0.22 percent which has *increased* the concentration of A as expected.

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Problem Solutions

Chapter 1 (Thermodynamic Systems)

Problem 1

Since the gas is expanding against a *constant* atmosphere (at pressure p) the total work L done by the gas can be written as

$$L = \int_{V_1}^{V_2} p dV = p(V_2 - V_1) \quad (328)$$

Using the numbers given in the text we have

$$L = 2.34 \text{ atm} (4.01 - 3.12) \text{ liters} = 2.082 \text{ atm liters} \quad (329)$$

To convert this result into CGS units (centimeters, grams, and seconds) we remember that

$$1 \text{ atm} = 1.01 \cdot 10^5 \text{ Pa} = 1.01 \cdot 10^5 \frac{\text{N}}{\text{m}^2} \quad (330)$$

$$1 \text{ liter} = 10^{-3} \text{ m}^3 \quad (331)$$

$$1 \text{ N} = 10^5 \text{ dyne} \quad (332)$$

$$1 \text{ m} = 100 \text{ cm} \quad (333)$$

Thus we have

$$1 \text{ atm liter} = 1.01 \cdot 10^5 \frac{\text{N}}{\text{m}^2} \times 10^{-3} \text{m}^3 \quad (334)$$

$$= 1.01 \cdot 10^2 \text{N m} \quad (335)$$

$$= 1.01 \cdot 10^2 \times 10^5 \text{dyne} \times 10^2 \text{cm} \quad (336)$$

$$= 1.01 \cdot 10^9 \text{dyne cm} . \quad (337)$$

After unit conversion, our total work L is given by

$$L = 2.103 \cdot 10^2 \text{N m} = 210.3 \text{N m} = 2.103 \cdot 10^9 \text{dyne cm} \quad (338)$$

Problem 2

Since we are told that the gas is hydrogen (H_2), looking to the periodic table gives us that hydrogen's mass per unit mole (molecular weight) is given by $M = 2\text{g/mole}$. The rest of the problem provides the gas's mass m , volume V , and temperature T as

$$m = 30 \text{g} \quad (339)$$

$$T = 18^\circ \text{C} = 18 + 273.15 = 291.15 \text{K} \quad (340)$$

$$V = 1 \text{m}^3 \quad (341)$$

Then one application of the ideal gas law

$$pV = \frac{m}{M}RT$$

gives

$$p = \frac{m}{M}RT \frac{1}{V} = \frac{30\text{g}}{2\text{g/mole}} \times 8.314 \frac{\text{J}}{\text{mole K}} \times 291.15 \text{K} \times \frac{1}{1\text{m}^3} = 3.63 \cdot 10^4 \frac{\text{J}}{\text{m}^3} \quad (342)$$

Since $1\text{J} = 1\text{N m}$, the above simplifies to

$$p = 3.64 \cdot 10^4 \frac{\text{N}}{\text{m}^2} = 3.64 \cdot 10^4 \text{Pa} . \quad (343)$$

To convert to atmospheres, requires the conversion to atmospheres from Pascals given by

$$1 \text{Pa} = \frac{1}{1.01 \cdot 10^5} \text{atm} = 9.9 \cdot 10^{-6} \text{atm} .$$

With this, the pressure in atmospheres becomes

$$p = 3.59 \cdot 10^{-1} \text{atm} . \quad (344)$$

Problem 3 (calculate the density and specific volume of nitrogen)

Nitrogen exists as a diatomic molecule (N_2) under standard conditions and thus has a molecular weight of

$$M = 2 \times 14 \text{ grams/mole} = 28 \text{ grams/mole} .$$

The ideal gas law gives for the density ρ

$$\rho \equiv \frac{m}{V} = \frac{Mp}{RT} . \quad (345)$$

In the problem, we are assuming that the Nitrogen is at 0 Celsius or 273.15 K. As such, the density will be completely determined once we have specified a pressure. Since none is given in this problem we will assume that atmospheric conditions apply and that the pressure is 1 atm = 1.01×10^5 Pa. With these assumptions the density is given by

$$\begin{aligned} \rho &= \frac{(28 \text{ grams/mole}) (1.01 \times 10^5 \text{ Pa})}{(8.314 \text{ J/mole K}) (273.15 \text{ K})} \\ &= 1244 \frac{\text{grams Pa}}{\text{J}} = 1244 \frac{(10^{-3} \text{ kg})(\text{kg/ms}^2)}{\text{kg m}^2/\text{s}^2} \\ &= 1.244 \frac{\text{kg}}{\text{m}^3} = 1.244 \times 10^{-3} \frac{\text{g}}{\text{cm}^3} . \end{aligned}$$

Since the specific volume is defined to be the reciprocal of the density, we have numerically that

$$v = \frac{1}{\rho} = 0.8038585 \frac{\text{m}^3}{\text{kg}} = 803.8585 \frac{\text{cm}^3}{\text{g}} . \quad (346)$$

Problem 4

From Fermi Eq. 9 in the book we have the work for an isothermal expansion is given by

$$L = \frac{m}{M} RT \log\left(\frac{V_2}{V_1}\right) = \frac{m}{M} RT \log\left(\frac{p_1}{p_2}\right) . \quad (347)$$

For this problem the provided inputs are

$$\begin{aligned} m &= 10 \text{ g} \\ M &= 32.0 \text{ g/mol} \\ R &= 8.314 \text{ J/molK} \\ T &= 20 \text{ C} = 293.15 \text{ K} \\ p_1 &= 1 \text{ atm} \\ p_2 &= 0.3 \text{ atm} \end{aligned}$$

with these inputs the expression for work above becomes

$$L = \left(\frac{10 \text{ g}}{32 \text{ g/mol}}\right) \left(8.314 \frac{\text{J}}{\text{molK}}\right) (293.15 \text{ K}) \log\left(\frac{1}{0.3}\right) \quad (348)$$

which simplify to

$$L = 916.9 \text{ J} . \quad (349)$$

Chapter 2 (The First Law of Thermodynamics)

Problem 1

From the first law of thermodynamics in canonical form ($dU = dQ - dW$) and the energy unit conversion between cal's and ergs of

$$1\text{cal} = 4.185 \cdot 10^7 \text{erg},$$

we obtain

$$dW = 3.4 \cdot 10^8 \text{erg} \quad (350)$$

$$dQ = 32 \text{cal} = 32(4.185 \cdot 10^7 \text{erg}) = 1.339 \cdot 10^9 \text{erg}. \quad (351)$$

From these we obtain for dU

$$dU = 1.339 \cdot 10^9 - 3.4 \cdot 10^8 = 9.9 \cdot 10^8 \text{erg} = 23.8 \text{cal} \quad (352)$$

Problem 2

The work done by an isothermal expansion is given by Fermi Eq. 9

$$L = \frac{m}{M} RT \log \left(\frac{p_1}{p_2} \right) = \frac{m}{M} RT \log \left(\frac{V_2}{V_1} \right). \quad (353)$$

Since $\frac{m}{M}$ is the number of moles of the gas under consideration for the specifics for this problem we have that

$$L = (3\text{mol})(8.314 \text{J/molK})(0 + 273.15 \text{K}) \log \left(\frac{5}{3} \right) = 3.48 \cdot 10^3 \text{J} = 831.54 \text{cal}.$$

Since we are considering an ideal gas whos internal energy is a function of temperature only the first law of thermodynamics $dU = dQ - dW$ simplifies since the expansion considered is isothermal ($dU = 0$) to give

$$dQ = dW.$$

Because of this relationship, we have that the number of calories absorbed, or Q , is given by $Q = W = L$ which is computed above.

Problem 3 (a straight line transformation in the (V, p) plane)

For this problem we desire to compute the amount of work performed by the gas when it undergoes a straight line transformation between (V_0, p_0) and (V_1, p_1) in the (V, p) plane. In the specific case given in this problem the initial and final volumes (and temperatures) are

specified while the initial and final pressures must be computed from the equation of state for an ideal gas. Using the ideal gas law to derive the corresponding pressure p_0 we have

$$p_0 = \frac{8.314 \text{ J/molK } 291 \text{ K } 1 \text{ mol}}{2.1 \cdot 10^{-2} \text{ m}^3} = 1.15 \cdot 10^5 \text{ Pa}.$$

In the same way we find

$$p_1 = 1.99 \cdot 10^5 \text{ Pa}.$$

Since we have not derived an expression for the work done under a straight line transformation in the (V, p) plane we do so now and then use its result to evaluate this problem. The work a gas performs under *any* transformation in the (V, p) plane is given by

$$W = L = \int p dV = \int p(V) dV.$$

Where we have expressed the path in the (V, p) plane as a *function* of V explicitly with the notation $p(V)$. When the path in the (V, p) plane is a *line* connecting the state (V_0, p_0) to (V_1, p_1) can derive an explicit formula for the path by equating the slope at any point on the line to the slope between the two end points as

$$\frac{p(V) - p_0}{V - V_0} = \frac{p_1 - p_0}{V_1 - V_0}.$$

On solving for $p = p(V)$ we obtain

$$p = p_0 + \frac{p_1 - p_0}{V_1 - V_0}(V - V_0).$$

Thus the work the gas must do as it traverses this path is given by the integral

$$L = \int_{V_0}^{V_1} \left(p_0 + \frac{p_1 - p_0}{V_1 - V_0}(V - V_0) \right) dV.$$

The algebra needed to perform this integration is

$$\begin{aligned} L &= p_0(V_1 - V_0) + \left(\left(\frac{p_1 - p_0}{V_1 - V_0} \right) \frac{(V - V_0)^2}{2} \right) \Big|_{V_0}^{V_1} = p_0(V_1 - V_0) + \left(\frac{p_1 - p_0}{V_1 - V_0} \right) \frac{(V_1 - V_0)^2}{2} \\ &= p_0(V_1 - V_0) + \frac{1}{2}(p_1 - p_0)(V_1 - V_0) = (V_1 - V_0) \left[p_0 + \frac{p_1}{2} - \frac{p_0}{2} \right] \\ &= \frac{1}{2}(V_1 - V_0)(p_1 + p_0). \end{aligned}$$

Now $V_1 - V_0 < 0$ and thus the work is negative and the *environment* performs work on the system. Note also that the absolute value of the above expression is the area of the triangle connecting the three states (V_0, p_0) , (V_1, p_1) , and (V_1, p_0) and the rectangle beneath this triangle. Evaluating the above with the given values of p and V gives

$$L = \frac{1}{2}(1.27 - 2.1) \cdot 10^{-2} \text{ m}^3 (1.99 + 1.15) \cdot 10^5 \text{ Pa} = -1.3 \cdot 10^3 \text{ m}^3 \text{ Pa}.$$

To calculate the heat absorbed by the system we remember that for an ideal gas $U(T) = C_V T$ and a diatomic gas specifically has $C_V = \frac{5}{2}R$ so we have the change in internal energy given by $\Delta U = C_V \Delta T = C_V(T_1 - T_0)$ or

$$\Delta U = C_V(305 - 291) = C_V(14 \text{ K}) = \frac{5}{2}(8.314 \text{ J/molK})(14 \text{ K})(1 \text{ mol}) = 2.9 \cdot 10^2 \text{ J}.$$

From the first law of thermodynamics for small changes we have $\Delta Q = \Delta U + \Delta W$ and we obtain for the heat absorbed by the system

$$\Delta Q = 2.9 \cdot 10^2 \text{J} + (-1.3 \cdot 10^3 \text{J}) = -10.1 \cdot 10^2 \text{J} = -1.01 \cdot 10^{10} \text{erg}.$$

Where we used the unit conversion between ergs and Joules of $1 \text{J} = 10^7 \text{erg}$.

Problem 4

In this problem we have one mole of a diatomic gas undergoing an adiabatic volume expansion. If we define the initial volume to be V_0 the final volume V_1 is then $1.35V_0$. For an adiabatic transformation we have

$$TV^{K-1} = \text{constant}. \quad (354)$$

Restricting this expression to connect the two states (T_0, V_0) and (T_1, V_1) we obtain

$$T_0 V_0^{K-1} = T_1 V_1^{K-1} \quad (355)$$

Solving for the final temperature T_1 gives

$$T_1 = T_0 \left(\frac{V_0}{V_1} \right)^{K-1}. \quad (356)$$

We are given the initial temperature of $T_0 = 18\text{C} = 18 + 273.15\text{K} = 291.15\text{K}$, the knowledge that the gas is diatomic (so $K = \frac{7}{5}$), and the fact that ratio of volumes is given by $\frac{V_0}{V_1} = \frac{1}{1.35}$. From this information we can compute that

$$\left(\frac{V_0}{V_1} \right)^{K-1} = 0.507. \quad (357)$$

With this we finally compute the final temperature as $T_1 = 291.15\text{K} (0.507) = 147.6 \text{K}$.

Chapter 3 (The Second Law of Thermodynamics)

Problem 1

Referring to figure, XXX, we first characterize what we know along each path in the p - V plane and then develop the necessary mathematics. First, paths BD and CA are adiabatic therefore no heat flows through them. Second, along AB and DC the temperature does not change and since for an ideal gas the internal energy U is a function of temperature only $U = U(T)$. Therefore along AB and DC $dU = 0$ so from the first law we have that $dQ = dW$ which implies $Q = W$.

We will solve this problem for the total work performed by the gas by computing the work along each path in a clockwise fashion beginning with the path AB. To perform this calculation we will require the work performed by an ideal gas along an adiabatic expansion. This will be calculated first and used in the calculations that follow.

We begin by deriving the work performed during an adiabatic transformation between two general points in $p - V$ space (p_1, V_1) and (p_2, V_2) . Along an adiabatic transformation of an ideal gas we have

$$pV^K = \text{constant}, \quad (358)$$

or anchoring the “constant” in the above expression to the point (p_1, V_1) we have

$$pV^k = p_1V_1^k \quad (359)$$

or solving for $p = p(V)$ we obtain

$$p = p_1 \left(\frac{V_1}{V} \right)^K = p_1 \left(\frac{V}{V_1} \right)^{-K} \quad (360)$$

Thus the work between two points can be calculated in a straight forward manner as

$$\begin{aligned} W_{12} &= \int_{V_1}^{V_2} p dV \\ &= \left(\frac{p_1}{V_1^{-k}} \right) \int_{V_1}^{V_2} V^{-k} dV \\ &= \left(\frac{p_1}{V_1^{-k}} \right) \frac{V^{-k+1}}{-k+1} \Big|_{V_1}^{V_2} \\ &= \frac{p_1 V_1^k}{1-k} (V_2^{-k+1} - V_1^{-k+1}). \end{aligned} \quad (361)$$

We now begin with the calculations required for this particular problem. First the work performed by our ideal gas along the isothermal path AB is given by

$$W_{AB} = RT_2 \log\left(\frac{V_B}{V_A}\right), \quad (362)$$

which when evaluated, using the numbers given in the problem, gives the following

$$W_{AB} = (8.314\text{J/molK})(400\text{K}) \log\left(\frac{5}{1}\right) = 5352.3\text{J}. \quad (363)$$

Note that this is also equal to the heat absorbed by our engine Q_2 , at this state of the cycle. Now along the path BD, since it is adiabatic we have in terms of variables of this problem

$$T_2 V_B^{K-1} = T_1 V_D^{K-1}. \quad (364)$$

Solving for V_D we have

$$V_D = \left(\frac{T_2}{T_1} V_B^{K-1} \right)^{1/K-1} = V_B \left(\frac{T_2}{T_1} \right)^{1/K-1}. \quad (365)$$

Using the numbers from the text, we get that

$$V_D = 5 \text{liters} \left(\frac{400}{300} \right)^{1/K-1}.$$

Now for a monotonic gas $K = 5/3$ giving the volume in the D state the value

$$V_D = 7.69 \text{ liter}.$$

Using equation 361 we have that for a monotonic gas

$$W_{BD} = \left(\frac{(6.65 \cdot 10^5 \text{Pa})(5 \cdot 10^{-3} \text{m}^3)^{5/3}}{1 - \frac{5}{3}} \right) \left((7.69 \cdot 10^{-3} \text{m}^3)^{1-\frac{5}{3}} - (5 \cdot 10^{-3} \text{m}^3)^{1-\frac{5}{3}} \right) = 1.24 \cdot 10^3 \text{J}.$$

For practice, the units in this expression work out as follows

$$\begin{aligned} \text{Pa m}^5 (\text{m}^3)^{-\frac{2}{3}} &= \text{Pa m}^5 \text{m}^{-2} \\ &= \text{Pa m}^3 \\ &= \frac{\text{N}}{\text{m}^2} \text{m}^3 \\ &= \text{N m} = \text{J} \end{aligned}$$

Along the isothermal path DC we have that $pV = \text{constant}$ giving in terms of the variables of this problem the expression

$$p_D V_D = p_C V_C, \quad (366)$$

which when we solve for p_C the expression

$$p_C = p_D \left(\frac{V_D}{V_C} \right) = 4.32 \cdot 10^5 \text{Pa} \left(\frac{7.69}{1.539} \right) = 2.158 \cdot 10^6 \text{Pa}. \quad (367)$$

Since CA is another adiabatic curve we have again that

$$T_2 V_A^{K-1} = T_1 V_C^{K-1},$$

or solving for V_C the expression

$$V_C = \left(\frac{T_2}{T_1} \right)^{1/K-1} V_A = 1 \text{ liter} \left(\frac{4}{3} \right)^{1/K-1} = 1.539 \text{ liter}. \quad (368)$$

Then the work along this segment of the cycle is given by

$$W_{CA} = RT_1 \log\left(\frac{V_D}{V_C}\right) = (8.314 \text{J/molK})(300 \text{K}) \log\left(\frac{7.69}{1.539}\right) = 4.01 \cdot 10^3 \text{J}. \quad (369)$$

Note that this equals the heat released by the process through this segment of the cycle or Q_1 . Finally, along the segment CA we have (using the expression for the work performed by an adiabatic transformation derived above) the following

$$L_{CA} = \left(\frac{2.158 \cdot 10^6 \text{Pa} (1.539 \cdot 10^{-3} \text{m}^3)^{5/3}}{\frac{5}{3}} \right) \left((10^{-3} \text{m}^3)^{-2/3} - (1.539 \cdot 10^{-3} \text{m}^3)^{-\frac{2}{3}} \right) = -1.65 \cdot 10^3 \text{J}$$

So the *total* work performed during the entire cycle is given by

$$W_{\text{total}} = W_{AB} + W_{BD} + W_{DC} + W_{CA} = 9.27 \cdot 10^3 \text{J} \quad (370)$$

Problem 2

First, convert the given temperatures into Kelvin as follows

$$T_1 = 18 \text{ C} = 291.15 \text{ K} \quad (371)$$

$$T_2 = 400 \text{ C} = 673.15 \text{ K}, \quad (372)$$

then using Fermi Eq. 59 we have a maximum possible efficiency between these two temperatures of

$$\eta = 1 - \frac{T_1}{T_2} = 1 - \frac{291.15}{673.15} = 0.567. \quad (373)$$

Problem 3

Converting the given temperatures into Kelvin we have

$$0 \text{ F} = 255.92 \text{ K} = T_1 \quad (374)$$

$$100 \text{ F} = 310.92 \text{ K} = T_2. \quad (375)$$

Then the minimum amount of work will be achieved when the engines operating cycle is reversible. As such, from Fermi Eq. 60. we have

$$L = \left(\frac{T_2 - T_1}{T_1} \right) Q_1. \quad (376)$$

With the heat extracted $Q_1 = 1 \text{ cal}$ we obtain, in various units

$$\begin{aligned} L &= 0.2149 Q_1 \\ &= 0.2149 \text{ cal} \\ &= 0.2149 \cdot 4.185 \cdot 10^7 \text{ erg} \\ &= 8.99 \cdot 10^6 \text{ erg} \\ &= 0.899 \text{ J}. \end{aligned}$$

Where in the above conversions we have used the conversion that $1 \text{ erg} = 10^{-7} \text{ J}$.

Chapter 4 (The Entropy)

Problem 1

We begin by recognizing that $1 \text{ kg H}_2\text{O} = 1000 \text{ gm H}_2\text{O}$ and converting the given temperatures to Kelvin as follows

$$\begin{aligned} T_1 &= 0 + 273.15 \text{ K} = 273.15 \text{ K} \\ T_2 &= 100 + 273.15 \text{ K} = 373.15 \text{ K} \end{aligned}$$

For liquid's I'll make the assumption that $C_p \approx C_V$ and is constant. As given in the book we will take its value to be 1cal/gm. A change in entropy along a reversible path is given by

$$\Delta S = \int_A^B \frac{dQ}{T}. \quad (377)$$

From the first law we have $dU = dQ - pdV$ and a constant volume transformation results in $dU = dQ = C_V dT$. Since along a constant volume transformation we have the heat ratio defined by

$$\left(\frac{dQ}{dT}\right)_V = C_V \quad (378)$$

Putting this expression into equation 377 results in

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V dT}{T} = C_V \ln\left(\frac{T_2}{T_1}\right). \quad (379)$$

Which is an expression to be understood as per unit mass. Using the numbers provided for this problem gives for the entropy change

$$\begin{aligned} \Delta S &= (1000 \text{ gm})(1\text{cal/gmK}) \ln\left(\frac{373.15}{273.15}\right) \\ &= 311.9 \text{ cal/K} = 311.9 (4.185 \cdot 10^7 \text{ erg/K}) \\ &= 1.305 \cdot 10^{10} \text{ erg/K} \end{aligned}$$

Problem 2

We are told that a body obeys the following equation of state

$$pV^{1.2} = 10^9 T^{1.1},$$

and asked to find the energy and entropy of such a system as a function of T and V . To solve this problem in a more general setting consider a body that has an equation of state given by

$$pV^a = dT^b \quad (380)$$

With $a = 1.2$, $d = 10^9$, $b = 1.1$, and $C_V = 0.1 \text{ cal/deg}$ for this problem. Now the units of V are liters. Now consider $U = U(V, T)$ then one can show for a system performing p - V work that

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p,$$

which is a nice expression because once an equation of state is specified empirically one can compute/evaluate

$$\left(\frac{\partial U}{\partial V}\right)_T,$$

by explicitly inserting the given equation of state. In our case

$$p = \frac{dT^b}{V^a}, \quad (381)$$

so the required derivative is given by

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{dbT^{b-1}}{V^a}, \quad (382)$$

therefore

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{dbT^{b-1}}{V^a} - \frac{dT^b}{V^a} = (b-1)\frac{dT^b}{V^a} = (b-1)p. \quad (383)$$

From this expression integrating U holding T fixed gives the following expression for $U(V, T)$, in terms of an arbitrary function of temperature C_1

$$U(V, T) = (b-1)dT^b \frac{V^{-a+1}}{-a+1} + C_1(T).$$

To evaluate $C_1(T)$ consider the definition of C_V (evaluated at $V_0 = 100$ liters)

$$C_V \equiv \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = (b-1)dbT^{b-1} \frac{V^{1-b}}{1-a} \Big|_{V_0} + C'_1(T).$$

which gives for $C'_1(T)$ the following

$$C'_V(T) = C_V - (b-1)dbT^{b-1} \frac{V_0^{1-b}}{1-a}.$$

Integrating with respect to T we get

$$C_1(T) = C_V T - (b-1)dT^b \frac{V_0^{1-b}}{1-a} + C_2$$

with C_2 a constant. Then $U(V, T)$ is given by

$$U(V, T) = C_V T + (b-1)dT^b \frac{(V^{1-a} - V_0^{1-a})}{1-a} + C_2 \quad (384)$$

To compute the entropy remember that for an reversible transformation we have

$$dS = \frac{dQ}{T} = \frac{dU + pdV}{T} = \frac{1}{T}dU + \frac{1}{T}pdV. \quad (385)$$

Using the expression for dU from differential calculus

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV,$$

in the above expression for dU we obtain for dS

$$dS = \frac{1}{T} \left[\left(C_V + (b-1) \frac{dbT^{b-1}}{1-a} (V^{1-a} - V_0^{1-a}) \right) dT + (b-1)dT^b V^{-a} dV \right] + \frac{1}{T} \frac{dT^b}{V^a} dV$$

or manipulating this expression we have

$$\begin{aligned}
dS &= \frac{C_V}{T}dT + \frac{(b_1)dbT^{b-2}}{1-a}(V^{1-a} - V_0^{1-a})dT + \frac{1}{T}(b-1)dT^bV^{-a}dV + \frac{1}{T}\frac{dT^b}{V^a}dV \\
&= C_V\frac{dT}{T} + \frac{bdT^bV^{-a}}{T}dV + \frac{b(b-1)T^{b-2}dV^{1-a}}{1-a}dT - \frac{(b-1)dbV_0^{1-a}T^{b-2}}{1-a}dT \\
&= C_V\frac{dT}{T} - \frac{(b-1)dbV_0^{1-a}T^{b-2}}{1-a}dT + bdT^{b-1}V^{-a}dV + \frac{d^2T^b}{dT^2}\frac{dV^{1-a}}{1-a}dT \\
&= C_V\frac{dT}{T} - b(b-1)d\frac{V_0^{1-a}}{1-a}T^{b-2}dT + \frac{d^2(T^b)}{dT^2}d\frac{V^{1-a}}{1-a}dT + d\frac{d(T^b)}{dT}V^{-a}dV
\end{aligned}$$

We can verify our algebra by checking if this is an exact differential as it must be. As such we must have

$$\frac{\partial}{\partial V} \left[\frac{C_V}{T} + \dots + \frac{d^2(T^b)}{dT^2}d\frac{V^{1-a}}{1-a} \right] = \frac{\partial}{\partial T} \left[d\frac{d(T^b)}{dT}V^{-a} \right]$$

which becomes

$$d\frac{d^2(T^b)}{dT^2}V^{-a} = d\frac{d^2(T^b)}{dT^2}V^{-a} \quad (386)$$

which is a true statement. Therefore one can integrate dS if one can find an integrating factor. Since dS is an exact differential there exists a function $S(T, V)$ such that

$$\left(\frac{\partial S}{\partial T} \right)_V = d\frac{d^2T^b}{dT^2}\frac{V^{1-a}}{1-a} + \frac{C_V}{T} - b(b-1)\frac{dV_0^{1-a}}{1-a}T^{b-2} \quad (387)$$

and

$$\left(\frac{\partial S}{\partial V} \right)_T = d\frac{d(T^b)}{dT}V^{-a}. \quad (388)$$

The second expression gives that

$$S = d\frac{d(T^b)}{dT}\frac{V^{1-a}}{1-a} + F(T), \quad (389)$$

for an arbitrary function $F(T)$. Taking the temperature derivative of the above gives

$$\left(\frac{\partial S}{\partial T} \right)_V = d\frac{d^2(T^b)}{dT^2}\frac{V^{-a}}{1-a} + F'(T)$$

and setting this equal to equation 387 gives for $F'(T)$

$$F'(T) = \frac{C_V}{T} - b(b-1)T^{b-2}\frac{V_0^{1-a}}{1-a}d$$

which can be integrated to give for $F(T)$

$$F(T) = C_V \ln(T) - bT^{b-1}\frac{V_0^{1-a}}{1-a}d + S_0.$$

In total we have for $S(T, V)$ the following

$$S(T, V) = C_V \ln(T) + \frac{dbT^{b-1}}{1-a}(V^{1-a} - V_0^{1-a}) + S_0 \quad (390)$$

Problem 3

From Clapeyron's equation we have

$$\frac{dp}{dT} = \frac{\lambda}{T(V_2 - V_1)} \quad (391)$$

Here V_2 is the specific volume of the gas phase and V_1 is the specific volume of liquid phase. In Kelvin, the boiling temperature for ethyl alcohol is given by $T = 351.45\text{K}$. Assuming $V_1 \ll V_2$ and that the value of V_2 for ethyl alcohol is approximately the same as for H_2O of $1677 \frac{\text{cm}^3}{\text{gm}}$ Clapeyron's equation becomes

$$\begin{aligned} \frac{dp}{dT} &= \frac{855 \frac{\text{J}}{\text{gm}}}{(351.45\text{K})(1677 \cdot 10^{-6} \frac{\text{m}^3}{\text{gm}})} \\ &= 1.45 \cdot 10^3 \frac{\text{J}}{\text{m}^3 \text{K}} \\ &= 1.45 \cdot 10^3 \frac{\text{Pa}}{\text{K}}. \end{aligned}$$

Chapter 5 (Thermodynamic Potentials)

Problem 1

WWX: I have not finished proofreading this section ... start this is page 11 from the second set of scanned notes

The phase rule $v = 2 + n - f$, saturated solution and a solid dissolved in the in the substitute have two phase liquid solution and solid (know this is correct page 86 gives examples of salt in H_2O and two components $n = 2$ (a solid and a liquid component).

$$v = 2 + 2 - 2 = 2 \quad (392)$$

therefore we can specify 2 variables T and p arbitrary. I would think that the correct answer would be T only. I know that increasing the temperature increases the solvability but am not sure about the pressure)

Problem 2

I am told the amounts of H_2O and air. I'll assume air contains N_2 , O_2 , and H_2 only and H_2O vapor, then f equals the number of phases (which is 2), and n equals the number of components which is 4. We have that

$$v = 2 + 4 - 2 = 4 \quad (393)$$

But we are told the amount of H_2O . and air so we are told

Problem 3

Now

$$v(t) = v_0 + v_1t + v_2t^2 \quad (394)$$

$$v_0 = 924 \quad (395)$$

$$v_1 = 0.0015 \quad (396)$$

$$v_2 = 0.0000061 \quad (397)$$

The units of T are centigrade, the units of V are volts, and the units of e are Columbs, from Page 96 we have

$$dQ = dU + dL = -eU(T) + ev(T) \quad (398)$$

but from the equation of Helmholtz $u(T) = v - T \frac{dv}{dT}$, thus the equation of Helmholtz gives the a functional form for the energy lost per unit charge.

$$u(T) = v_0 + v_1t + v_2t^2 - T(v_1 + 2v_2t) \quad (399)$$

$$= (v_0 + Tv_1) + (v_1 - 2v_2T)t + v_2t^2 \quad (400)$$

Then $dQ = -e(v - T \frac{dv}{dT}) + ev = eT \frac{dv}{dT}$ therefore we need $u(T)$ actually

$$\Delta Q = eT \frac{dv}{dT} = eT(v_1 + 2v_2t) \quad (401)$$

Chapter 6 (Gaseous Reactions)

Chapter 7 (The Thermodynamics of Dilute Solutions)

Chapter 8 (The Entropy Constant)

WWX: I have not finished this section ... end