INTRODUCTORY CHEMICAL ENGINEERING THERMODYNAMICS

SECOND EDITION

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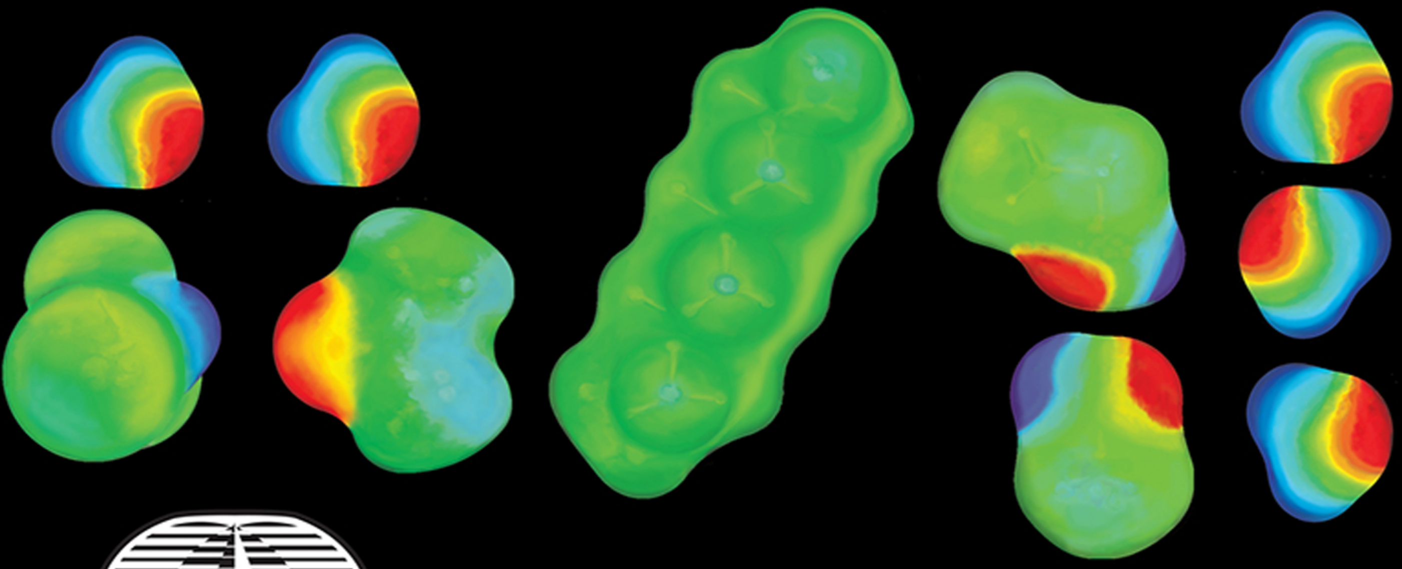

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Introductory Chemical Engineering Thermodynamics, Second Edition

Example 6.10 Application of the triple product relation

Evaluate $(\partial S/\partial V)_A$ in terms of C_P, C_V, T, P, and V. Your answer may include absolute values of S if it is not a derivative constraint or within a derivative term.

Solution: This problem illustrates a typical situation where the triple product rule is helpful because the Helmholtz energy is held constant (hint #2). It is easiest to express changes in the Helmholtz energies as changes in other variables. Applying the triple product rule:

$$(\partial S/\partial V)_A = -(\partial A/\partial V)_S / (\partial A/\partial S)_V$$

Applying the expansion rule twice, $dA = -PdV - SdT \Rightarrow (\partial A/\partial V)_S = -P - S(\partial T/\partial V)_S$ and $(\partial A/\partial S)_V = 0 - S(\partial T/\partial S)_V$. Recalling Eqn. 4.30 and converting to measurable derivatives:

$$\Rightarrow \left(\frac{\partial T}{\partial S}\right) = \frac{T}{C_V} \text{ and } (\partial T/\partial V)_S = \left(\frac{\partial T}{\partial S}\right)_V \left(\frac{\partial S}{\partial V}\right)_T = -\frac{T}{C_V}\left(\frac{\partial P}{\partial T}\right)_V$$

Substituting:

$$\Rightarrow \left(\frac{\partial S}{\partial V}\right)_A = \frac{-PC_V}{ST} + \left(\frac{\partial P}{\partial T}\right)_v$$

Example 6.11 Master equation for an ideal gas

Derive a master equation for calculating changes in U for an ideal gas in terms of $\{V, T\}$.

Solution:

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

Applying results of the previous examples:

$$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV \qquad 6.52$$

Notice that this expression is more complicated than the fundamental property relation in terms of $\{S, V\}$. As we noted earlier, this is why $\{S, V\}$ are the natural variables for dU, rather than $\{T, V\}$ or any other combination. For an ideal gas, we can use the results of Example 6.6 to find:

$$dU^{ig} = C_V^{ig} dT \qquad \text{(ig) } 6.53$$

Example 6.12 Relating C_P to C_V

Derive a general formula to relate C_P and C_V.

Solution: Start with an expression that already contains one of the desired derivatives (e.g., C_V) and introduce the variables necessary to create the second derivative (e.g., C_P). Beginning with Eqn. 6.38,

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

and using the expansion rule with T at constant P,

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_V}{T}\cancelto{1}{\left(\frac{\partial T}{\partial T}\right)_P} + \left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P \text{, where the left-hand side is } \frac{C_P}{T}.$$

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

Exercise:
Verify that the last term simplifies to R for an ideal gas.

Owing to all the interrelations between all the derivatives, there is usually more than one way to derive a useful result. This can be frustrating to the novice. Nevertheless, patience in attacking the problems, and attacking a problem from different angles, can help you to visualize the structure of the calculus in your mind. Each problem is like a puzzle that can be assembled in multiple ways. Patience in developing these tools is rewarded with a mastery of the relations that permit quick insight into the easiest way to solve problems.

6.3 ADVANCED TOPICS

Hints for Remembering the Auxiliary Relations

Auxiliary relations can be easily written by memorizing the fundamental relation for dU and the natural variables for the other properties. Note that $\{T,S\}$ and $\{P,V\}$ always appear in pairs, and each pair is a set of conjugate variables. A Legendre transformation performed on internal energy among conjugate variables changes the dependent variable and the sign of the term involving the conjugate variables. For example, to transform P and V, the product PV is added to U, resulting in Eqn. 6.5. To transform T and S, the product TS is subtracted: $A = U - TS$, $dA = dU - TdS - SdT = -SdT - PdV$. The pattern can be easily seen in the "Useful Derivatives" table on the front book end paper. Note that $\{T,S\}$ always appear together, and $\{P,V\}$ always appear together, and the sign changes upon transformation.

Jacobian Method of Derivative Manipulation

A partial derivative may be converted to derivatives of measurable properties with any two desired independent variables from the set $\{P,V,T\}$. Jacobian notation can be used to manipulate partial derivatives, and there are several useful rules for manipulating derivatives with the notation. The

Joule-Thomson coefficient is a derivative that indicates how temperature changes upon pressure change at fixed enthalpy, $\left(\frac{\partial T}{\partial P}\right)_H$, which is written in Jacobian notation as $\left(\frac{\partial T}{\partial P}\right)_H = \frac{\partial(T, H)}{\partial(P, H)}$. Note how the constraint of constant enthalpy is incorporated into the notation. The rules for manipulation of the Jacobian notation are,

1. Jacobian notation represents a determinant of partial derivatives,

$$\frac{\partial(K, L)}{\partial(X, Y)} = \left(\frac{\partial K}{\partial X}\right)_Y\left(\frac{\partial L}{\partial Y}\right)_X - \left(\frac{\partial K}{\partial Y}\right)_X\left(\frac{\partial L}{\partial X}\right)_Y = \begin{vmatrix} \left(\frac{\partial K}{\partial X}\right)_Y & \left(\frac{\partial K}{\partial Y}\right)_X \\ \left(\frac{\partial L}{\partial X}\right)_Y & \left(\frac{\partial L}{\partial Y}\right)_X \end{vmatrix} \tag{6.54}$$

   The Jacobian is particularly simple when the numerator and denominator have a common variable,

$$\frac{\partial(K, L)}{\partial(X, L)} = \left(\frac{\partial K}{\partial X}\right)_L \tag{6.55}$$

   which is a special case of Eqn. 6.54.

2. When the order of variables in the numerator or denominator is switched, the sign of the Jacobian changes. Switching the order of variables in both the numerator and denominator results in no sign change due to cancellation. Consider switching the order of variables in the numerator,

$$\frac{\partial(K, L)}{\partial(X, Y)} = -\frac{\partial(L, K)}{\partial(X, Y)} \tag{6.56}$$

3. The Jacobian may be inverted.

$$\frac{\partial(K, L)}{\partial(X, Y)} = \left[\frac{\partial(X, Y)}{\partial(K, L)}\right]^{-1} = \frac{1}{\dfrac{\partial(X, Y)}{\partial(K, L)}} \tag{6.57}$$

4. Additional variables may be interposed. When additional variables are interposed, it is usually convenient to invert one of the Jacobians.

$$\frac{\partial(K, L)}{\partial(X, Y)} = \frac{\partial(K, L)}{\partial(B, C)}\frac{\partial(B, C)}{\partial(X, Y)} = \frac{\dfrac{\partial(K, L)}{\partial(B, C)}}{\dfrac{\partial(X, Y)}{\partial(B, C)}} \tag{6.58}$$

Manipulation of Derivatives

Before manipulating derivatives, the desired independent variables are selected. The selected independent variables will be held constant outside the derivatives in the final formula. The general procedure is to interpose the desired independent variables, rearrange as much as possible to obtain Jacobians with common variables in the numerator and denominator, write the determinant for any

Jacobians without common variables; then use Maxwell relations, the expansion rule, and so on, to simplify the answer.

1. If the starting derivative already contains both the desired independent variables, the result of Jacobian manipulation is redundant with the triple product rule. The steps are: 1) write the Jacobian; 2) interpose the independent variables; 3) rearrange to convert to partial derivatives.

   Example: Convert $\left(\frac{\partial T}{\partial P}\right)_H$ to derivatives that use T and P as independent variables.

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{\partial(T,H)}{\partial(P,H)} = \frac{\partial(T,H)}{\partial(T,P)}\frac{\partial(T,P)}{\partial(P,H)} = \frac{\dfrac{\partial(H,T)}{\partial(P,T)}}{-\dfrac{\partial(H,P)}{\partial(T,P)}} = \frac{-\left(\dfrac{\partial H}{\partial P}\right)_T}{\left(\dfrac{\partial H}{\partial T}\right)_P} = \frac{-\left(\dfrac{\partial H}{\partial P}\right)_T}{C_P}$$

   and the numerator can be simplified using the expansion rule as presented in Example 6.1.

2. If the starting derivative has just one of the desired independent variables, the steps are: 1) write the Jacobian; 2) interpose the desired variables; 3) write the determinant for the Jacobian without a common variable; 4) rearrange to convert to partial derivatives.

   Example: Find a relation for the adiabatic compressibility, $\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S$ in terms of derivatives using T, P as independent variables.

$$\left(\frac{\partial V}{\partial P}\right)_S = \frac{\partial(V,S)}{\partial(P,S)} = \frac{\partial(V,S)}{\partial(P,T)}\frac{\partial(P,T)}{\partial(P,S)} = \left[\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial S}{\partial T}\right)_P - \left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial S}{\partial P}\right)_T\right]\left(\frac{\partial T}{\partial S}\right)_P$$

   Now, including a Maxwell relation as we simplify the second term in square brackets, and then combining terms:

$$\left(\frac{\partial V}{\partial P}\right)_S = \left(\frac{\partial V}{\partial P}\right)_T + \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P^2$$

$$\kappa_S = -\frac{1}{V}\left(\left(\frac{\partial V}{\partial P}\right)_T + \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P^2\right) = \kappa_T - \frac{T}{VC_P}\left(\frac{\partial V}{\partial T}\right)_P^2$$

3. If the starting derivative has neither of the desired independent variables, the steps are: 1) write the Jacobian; 2) interpose the desired variables; 3) write the Jacobians as a quotient and write the determinants for both Jacobians; 4) rearrange to convert to partial derivatives.

   Example: Find $\left(\frac{\partial S}{\partial V}\right)_U$ in measurable properties using P and T as independent variables.

$$\frac{\partial(S,U)}{\partial(V,U)} = \frac{\partial(S,U)}{\partial(P,T)}\frac{\partial(P,T)}{\partial(V,U)} = \frac{\dfrac{\partial(S,U)}{\partial(P,T)}}{\dfrac{\partial(V,U)}{\partial(P,T)}}$$

   Writing the determinants for both Jacobians:

$$\frac{\left(\frac{\partial S}{\partial P}\right)_T\left(\frac{\partial U}{\partial T}\right)_P-\left(\frac{\partial U}{\partial P}\right)_T\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial U}{\partial T}\right)_P-\left(\frac{\partial U}{\partial P}\right)_T\left(\frac{\partial V}{\partial T}\right)_P}$$

Now, using the expansion rule for the derivatives of *U,* and also introducing Maxwell relations,

$$\frac{-\left(\frac{\partial V}{\partial T}\right)_P\left[C_P-P\left(\frac{\partial V}{\partial T}\right)_P\right]+\frac{C_P}{T}\left[T\left(\frac{\partial V}{\partial T}\right)_P+P\left(\frac{\partial V}{\partial P}\right)_T\right]}{\left(\frac{\partial V}{\partial P}\right)_T\left[C_P-P\left(\frac{\partial V}{\partial T}\right)_P\right]+T\left(\frac{\partial V}{\partial T}\right)_P^2+P\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial V}{\partial T}\right)_P}=$$

$$\frac{P\left(\frac{\partial V}{\partial T}\right)_P^2+C_P\frac{P}{T}\left(\frac{\partial V}{\partial P}\right)_T}{T\left(\frac{\partial V}{\partial T}\right)_P^2+C_P\left(\frac{\partial V}{\partial P}\right)_T}=\frac{P}{T}$$

The result is particularly simple. We could have derived this directly if we had recognized that S and V are the natural variables for U. Therefore, $dU = TdS - P\ dV = 0$, $TdS|_U = -PdV|_U$, $T\left(\frac{\partial S}{\partial V}\right)_U = P$, $\left(\frac{\partial S}{\partial V}\right)_U = \frac{P}{T}$. However, the exercise demonstrates the procedure and power of the Jacobian technique even though the result will usually not simplify to the extent of this example.

6.4 SUMMARY

We have seen in this chapter that calculus provides powerful tools permitting us to calculate changes in immeasurable properties in terms of other measurable properties. We started by defining additional convenience functions *A*, and *G* by performing Legendre transforms. We then reviewed basic calculus identities and extended throughout the remainder of the chapter. The ability to perform these manipulations lays the foundation for the development of general methods to calculate thermodynamic properties for any chemical from *P-V-T* relations. If we only had a general relation that perfectly described $P=P(V,T)$ for all the chemicals in the universe, it could be combined with the tools in this chapter to compute any property required by the energy and entropy balances. At present, no such perfect equation exists. This means that we need to understand what makes it so difficult to develop such an equation and how the various available equations can be applied in various situations to achieve reasonable and continuously improving estimates.

Important Equations

The procedures developed in this chapter are what is important. They provide a basis for transforming one set of derivatives into another and for thinking systematically about how variables relate to one another. The basic identities 6.11–6.17 combine with the fundamental properties for the remainder of the chapter. Nevertheless, several equations stand out as a summary of the results that can be rearranged to a desired form relatively quickly. These are the Maxwell Eqns. 6.29–6.32, and also some intermediate manipulations 6.37–6.41. They are included on the front flap of the textbook for your convenience.

Test Yourself

1. What are the restrictions necessary to calculate one state property in terms of only two other state variables?
2. When integrating Eqn. 6.53, under what circumstances may C_V be taken out of the integral?
3. May Eqn. 6.53 be applied to a condensed phase?
4. Is the heat capacity different for liquid acetone than for acetone vapor?
5. Can the tabulated heat capacities be used in Eqn. 6.53 for gases at high pressure?

6.5 PRACTICE PROBLEMS

P6.1 Express in terms of P, V, T, C_P, C_V, and their derivatives. Your answer may include absolute values of S if it is not a derivative constraint or within a derivative.

(a) $(\partial H/\partial S)_V$
(b) $(\partial H/\partial P)_V$
(c) $(\partial G/\partial H)_P$
(ANS. (a) $T[1+V/C_V(\partial P/\partial T)_v]$ (b) $C_v(\partial T/\partial P)_v+V$ (c) $-S/C_P$)

6.6 HOMEWORK PROBLEMS

6.1 Nitrogen (N_2) at 0.1 MPa and $T > 150$ K approximates ideal gas behavior. At $T < 300$ K, the covalent bond is fairly rigid, so the higher heat capacity relative to a spherical molecule results from the possibility of rotation. That is, since the molecule is linear, spinning around its axis does not generate any momentum, but rotating perpendicular to its axis can generate momentum in the two other dimensions. So the heat capacity is $C_V/R \sim 3/2 + 2/2 = 5/2$ at room temperature. As the temperature increases, vibrations begin to absorb energy, analogous to the Einstein solid, but the covalent bond can only vibrate in one dimension. Use the NIST WebBook to obtain data for N_2 at 0.1 MPa and T=[150, 2000 K]. Regress an optimal value for ε_q/k of N_2 and plot a comparison of the calculated results to experimental data.

6.2 Express in terms of P, V, T, C_P, C_V, and their derivatives. Your answer may include absolute values of S if it is not a derivative constraint or within a derivative.

(a) $(\partial G/\partial P)_T$
(b) $(\partial P/\partial A)_V$
(c) $(\partial T/\partial P)_S$
(d) $(\partial H/\partial T)_U$
(e) $(\partial T/\partial H)_S$
(f) $(\partial A/\partial V)_P$
(g) $(\partial T/\partial P)_H$
(h) $(\partial A/\partial S)_P$
(i) $(\partial S/\partial P)_G$

6.3 Express the following in terms of $U, H, S, A,$ and their derivatives.