

9.1: The Total Differential

In [Chapter 8](#) we learned that partial derivatives indicate how the dependent variable changes with one particular independent variable keeping the others fixed. In the context of an equation of state $P = P(T, V, n)$, the partial derivative of P with respect to V at constant T and n is:

$$\left(\frac{\partial P}{\partial V}\right)_{T,n}$$

and physically represents how the pressure varies as we change the volume at constant temperature and constant n .

The partial derivative of P with respect to T at constant V and n is:

$$\left(\frac{\partial P}{\partial T}\right)_{V,n}$$

and physically represents how the pressure varies as we change the temperature at constant volume and constant n .

What happens with the dependent variable (in this case P) if we change two or more independent variables simultaneously? For an infinitesimal change in volume and temperature, we can write the change in pressure as:

$$dP = \left(\frac{\partial P}{\partial V}\right)_{T,n} dV + \left(\frac{\partial P}{\partial T}\right)_{V,n} dT \quad (9.1.1)$$

Equation [9.1.1](#) is called the *total differential of P* , and it simply states that the change in P is the sum of the individual contributions due to the change in V at constant T and the change in T at constant V . This equation is true for infinitesimal changes. If the changes are not infinitesimal we will integrate this expression to calculate the change in P .[\[differentials_position1\]](#)

Let's now consider the volume of a fluid, which is a function of pressure, temperature and the number of moles: $V = V(n, T, P)$. The total differential of V , by definition, is:

$$dV = \left(\frac{\partial V}{\partial T}\right)_{P,n} dT + \left(\frac{\partial V}{\partial P}\right)_{T,n} dP + \left(\frac{\partial V}{\partial n}\right)_{T,P} dn \quad (9.1.2)$$

If we want to calculate the change in volume in a fluid upon small changes in P , T and n , we could use:

$$\Delta V \approx \left(\frac{\partial V}{\partial T}\right)_{P,n} \Delta T + \left(\frac{\partial V}{\partial P}\right)_{T,n} \Delta P + \left(\frac{\partial V}{\partial n}\right)_{T,P} \Delta n \quad (9.1.3)$$

Of course, if we know the function $V = V(n, T, P)$, we could also calculate ΔV as $V_f - V_i$, where the final and initial volumes are calculated using the final and initial values of P , T and n . This seems easy, so why do we need to bother with Equation [9.1.3](#)? The reason is that sometimes we can measure the partial derivatives experimentally, but we do not have an equation of the type $V = V(n, T, P)$ to use. For example, the following quantities are accessible experimentally and tabulated for different fluids and materials (Fig. [\[fig:diff_tables\]](#)):

- $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_{P,n}$ (coefficient of thermal expansion)
- $\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_{T,n}$ (isothermal compressibility)[\[differentials:compressibility\]](#)
- $V_m = \left(\frac{\partial V}{\partial n}\right)_{P,T}$ (molar volume)

Using these definitions, Equation [9.1.2](#) becomes:

$$dV = \alpha V dT - \kappa V dP + V_m dn \quad (9.1.4)$$

You can find tables with experimentally determined values of α and κ under different conditions, which you can use to calculate the changes in V . Again, as we will see later in this chapter, this equation will need to be integrated if the changes are not small. In any case, the point is that you may have access to information about the derivatives of the function, but not to the function itself (in this case V as a function of T , P , n).

In general, for a function $u = u(x_1, x_2, \dots, x_n)$, we define the total differential of u as:

$$du = \left(\frac{\partial u}{\partial x_1} \right)_{x_2 \dots x_n} dx_1 + \left(\frac{\partial u}{\partial x_2} \right)_{x_1, x_3 \dots x_n} dx_2 + \dots + \left(\frac{\partial u}{\partial x_n} \right)_{x_1 \dots x_{n-1}} dx_n \quad (9.1.5)$$

✓ Example 9.1.1

Calculate the total differential of the function $z = 3x^3 + 3yx^2 + xy^2$.

Solution

By definition, the total differential is:

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy$$

For the function given in the problem,

$$\left(\frac{\partial z}{\partial x} \right)_y = 9x^2 + 6xy + y^2$$

and

$$\left(\frac{\partial z}{\partial y} \right)_x = 3x^2 + 2xy$$

and therefore,

$$dz = (9x^2 + 6xy + y^2)dx + (3x^2 + 2xy)dy$$

COMPRESSIBILITY AND EXPANSION COEFFICIENTS OF LIQUIDS

This table gives data on the variation of the density of some common liquids with pressure and temperature. The pressure dependence is described to first order by the isothermal compressibility coefficient κ defined as

$$\kappa = -(1/V) (\partial V / \partial P)_T$$

where V is the volume, and the temperature dependence by the cubic expansion coefficient α ,

$$\alpha = (1/V) (\partial V / \partial T)_P$$

Substances are listed by molecular formula in the Hill order. More precise data on the variation of density with temperature over a wide temperature range can be found in Reference 1.

References

1. Lide, D. R., and Kehiaian, H. V., *CRC Handbook of Thermophysical and Thermochemical Data*, CRC Press, Boca Raton, FL, 1994.
2. Le Neindre, B., *Effets des Hautes et Très Hautes Pressions*, in *Techniques de l'Ingénieur*, Paris, 1991.
3. *Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, New Series, IV/4, High-Pressure Properties of Matter*, Springer-Verlag, Heidelberg, 1981.
4. Riddick, J. A., Bunger, W. B., and Sliko, T. K., *Organic Solvents, Fourth Edition*, John Wiley & Sons, New York, 1986.
5. Isaacs, N. S., *Liquid Phase High Pressure Chemistry*, John Wiley, New York, 1981.

Molecular formula	Name	Isothermal compressibility		Cubic expansion coefficient	
		$t/^\circ\text{C}$	$\kappa \times 10^3/\text{MPa}^{-1}$	$t/^\circ\text{C}$	$\alpha \times 10^3/^\circ\text{C}^{-1}$
Cl ₃ P	Phosphorus trichloride	20	9.45	20	1.9
H ₂ O	Water	20	4.591	20	0.206
		25	4.524	25	0.256
		30	4.475	30	0.302
Hg	Mercury	20	0.401	20	0.1811
CCl ₄	Tetrachloromethane	20	10.50	20	1.14
		40	12.20	40	1.21
		70	15.6	70	1.33
CHBr ₃	Tri bromomethane	50	8.76	25	0.91
CHCl ₃	Trichloromethane	20	9.96	20	1.21
		50	12.9	50	1.33
CH ₂ Br ₂	Dibromomethane	27	6.85		
CH ₂ Cl ₂	Dichloromethane	25	10.3	25	1.39
CHI ₃	Iodomethane	27	10.3	25	1.26
CH ₃ O	Methanol	20	12.14	20	1.49
		40	13.83	40	1.59
CS ₂	Carbon disulfide	20	9.38	20	1.12
		40	10.6	35	1.16
C ₂ Cl ₄	Tetrachloroethylene	25	7.56	25	1.02
C ₂ HCl ₃	Trichloroethylene	25	8.57	25	1.17
C ₂ H ₂ Cl ₂	<i>trans</i> -1,2-Dichloroethylene	25	11.2	25	1.36
C ₂ H ₃ Cl ₃	1,1-Dichloroethane	20	7.97	25	0.93
C ₂ H ₄ Cl ₂	1,2-Dichloroethane	30	8.46	20	1.14
C ₂ H ₃ O ₂	Acetic acid	20	9.08	20	1.08
		80	13.7	80	1.38
C ₂ H ₅ Br	Bromomethane	20	11.53	20	1.31
C ₂ H ₅ I	Iodoethane	20	9.82	25	1.17
C ₂ H ₅ O	Ethanol	20	11.19	20	1.40
		70	15.93	70	1.67
C ₂ H ₄ O ₂	Ethylene glycol	20	3.64	20	0.626
C ₂ H ₄ O	Acetone	20	12.62	20	1.46
		40	15.6	40	1.57
C ₃ H ₇ Br	1-Bromopropane	0	10.22	25	1.2
C ₃ H ₇ Cl	1-Chloropropane	0	12.09	20	1.4
C ₃ H ₇ I	1-Iodopropane	0	10.22	25	1.09
C ₃ H ₇ O	1-Propanol	0	8.43	0	1.22
C ₃ H ₇ O	2-Propanol	40	13.32	40	1.55
C ₃ H ₈ O ₂	1,2-Propanediol	0	4.45	20	0.695
C ₃ H ₈ O ₂	1,3-Propanediol	0	4.09	20	0.61
C ₃ H ₈ O ₃	Glycerol	0	2.54	20	0.520

VOLUMETRIC PROPERTIES OF AQUEOUS SODIUM CHLORIDE SOLUTIONS

This table gives the following properties of aqueous solutions of NaCl as a function of temperature and concentration: All data refer to a pressure of 100 kPa (1 bar). The reference gives properties over a wider range of temperature and pressure.

Specific volume v (reciprocal of density) in cm^3/g
 Isothermal compressibility $\kappa_T = -(1/v)(\partial v/\partial P)_T$ in GPa^{-1}
 Cubic expansion coefficient $\alpha_v = (1/v)(\partial v/\partial T)_P$ in K^{-1}

Reference

Rogers, P. S. Z., and Pitzer, K. S., *J. Phys. Chem. Ref. Data*, 11, 15, 1982.

$t/^\circ\text{C}$	0.100	0.250	0.500	Molality in mol/kg					
				0.750	1.000	2.000	3.000	4.000	5.000
Specific volume v in cm^3/g									
0	0.995732	0.989259	0.978889	0.968991	0.959525	0.925426	0.896292	0.870996	0.848646
10	0.995998	0.989781	0.979804	0.970256	0.961101	0.927905	0.899262	0.874201	0.851958
20	0.997620	0.991564	0.981833	0.972505	0.963544	0.930909	0.902565	0.877643	0.855469
25	0.998834	0.992832	0.983185	0.973932	0.965038	0.932290	0.904339	0.879457	0.857301
30	1.000279	0.994319	0.984735	0.975539	0.966694	0.934382	0.906194	0.881334	0.859185
40	1.003796	0.997883	0.988374	0.979243	0.970455	0.938287	0.910145	0.885276	0.863108
50	1.008064	1.002161	0.992668	0.983551	0.974772	0.942603	0.914411	0.889473	0.867241
60	1.0130	1.0071	0.9976	0.9885	0.9797	0.9474	0.9191	0.8940	0.8716
70	1.0186	1.0127	1.0031	0.9939	0.9851	0.9526	0.9240	0.8987	0.8762
80	1.0249	1.0188	1.0092	0.9999	0.9909	0.9581	0.9293	0.9037	0.8809
90	1.0317	1.0256	1.0157	1.0063	0.9972	0.9640	0.9348	0.9089	0.8858
100	1.0391	1.0329	1.0228	1.0133	1.0040	0.9703	0.9406	0.9144	0.8910
Isothermal Compressibility κ_T in GPa^{-1}									
0	0.503	0.492	0.475	0.459	0.443	0.389	0.346	0.315	0.294
10	0.472	0.463	0.449	0.436	0.423	0.377	0.341	0.313	0.294
20	0.453	0.446	0.433	0.422	0.411	0.371	0.338	0.313	0.294
25	0.447	0.440	0.428	0.417	0.407	0.369	0.337	0.313	0.294
30	0.443	0.436	0.425	0.414	0.404	0.367	0.337	0.313	0.294
40	0.438	0.432	0.421	0.411	0.401	0.367	0.338	0.315	0.296
50	0.438	0.431	0.421	0.411	0.402	0.369	0.340	0.317	0.299
60	0.44	0.44	0.43	0.42	0.41	0.38	0.35	0.32	0.30
70	0.45	0.44	0.43	0.42	0.42	0.38	0.36	0.33	0.31
80	0.46	0.45	0.44	0.43	0.43	0.39	0.37	0.34	0.32
90	0.47	0.47	0.46	0.45	0.44	0.41	0.38	0.35	0.33
100	0.49	0.48	0.47	0.46	0.45	0.42	0.39	0.37	0.34
Cubic expansion coefficient α_v in K^{-1}									
0	-0.058	-0.026	0.024	0.069	0.110	0.237	0.313	0.355	
10	0.102	0.123	0.156	0.186	0.213	0.297	0.349	0.380	
20	0.218	0.232	0.254	0.274	0.292	0.349	0.384	0.406	
25	0.267	0.278	0.296	0.312	0.327	0.373	0.401	0.420	
30	0.311	0.320	0.334	0.347	0.359	0.395	0.418	0.433	
40	0.389	0.394	0.402	0.410	0.417	0.438	0.451	0.460	
50	0.458	0.460	0.464	0.467	0.470	0.479	0.484	0.486	
60	0.52	0.52	0.52	0.52	0.52	0.52	0.52	0.52	
70	0.58	0.58	0.58	0.57	0.57	0.56	0.55	0.54	
80	0.64	0.63	0.63	0.62	0.61	0.60	0.58	0.56	
90	0.69	0.68	0.67	0.67	0.66	0.63	0.61	0.59	
100	0.74	0.73	0.72	0.71	0.70	0.66	0.64	0.61	

Figure 9.1.1: Tables of isothermal compressibilities and expansion coefficients of different fluids (top) and sodium chloride solutions (bottom). Source: CRC Handbook of Physics and Chemistry (CC BY-NC-SA; Marcia Levitus)

Want to see more examples?

- Example 1: <http://www.youtube.com/watch?v=z0TxZ0EHZlg> Notice that she calls it 'the differential', but I prefer 'the total differential'.

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