

so we have

$$\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V} \right) = 0 \implies \frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T} \right) = \frac{\partial C_V}{\partial V} = 0,$$

which shows that C_V is independent of V .

4. Using Maxwell's relations.

Show that $(\partial H/\partial p)_T = V - T(\partial V/\partial T)_p$.

Start with $dH = T dS + V dp$.

Now divide by dp , holding T constant:

$$\frac{dH}{dp} \quad [\text{at constant } T] = \left(\frac{\partial H}{\partial p} \right)_T = T \left(\frac{\partial S}{\partial p} \right)_T + V.$$

Use the Maxwell relation (Table 9.1 of the text),

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

to get the result

$$\left(\frac{\partial H}{\partial p} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_p + V.$$

5. Pressure dependence of the heat capacity.

(a) Show that, in general, for quasi-static processes,

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_p.$$

(b) Based on (a), show that $(\partial C_p / \partial p)_T = 0$ for an ideal gas.

(a) Begin with the definition of the heat capacity,

$$C_p = \frac{\delta q}{dT} = T \frac{dS}{dT},$$

for a quasi-static process. Take the derivative:

$$\left(\frac{\partial C_p}{\partial p}\right)_T = T \left(\frac{\partial^2 S}{\partial p \partial T}\right) = T \left(\frac{\partial^2 S}{\partial T \partial p}\right) \quad (1)$$

since S is a state function. Substitute the Maxwell relation

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

into Equation (1) to get

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_p.$$

(b) For an ideal gas, $V(T) = NkT/p$, so

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{Nk}{p},$$

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_p = 0,$$

and therefore, from part (a),

$$\left(\frac{\partial C_p}{\partial p}\right)_T = 0.$$

$$(a) \quad dU = T dS + P dV + \mu dN + F dx,$$

$$dG = -S dT + V dP + F dx,$$

$$F = \left(\frac{\partial G}{\partial x} \right)_{T,P},$$

$$G(x) = \int (aT + b)x dx = \frac{1}{2}(aT + b)x^2.$$

$$(b) \quad \left(\frac{\partial S}{\partial x} \right)_{T,P} = - \left(\frac{\partial F}{\partial T} \right)_{x,P},$$

$$(c) \quad \left(\frac{\partial S}{\partial x} \right)_{T,P} = - \left(\frac{\partial F}{\partial T} \right)_{x,P} = -ax,$$

$$S(x) = \int -ax dx = -\frac{1}{2}ax^2.$$

$$(d) \quad F = \left(\frac{\partial G}{\partial x} \right)_{T,P} = \left(\frac{\partial H}{\partial x} \right)_{T,P} - T \left(\frac{\partial S}{\partial x} \right)_{T,P} = \left(\frac{\partial H}{\partial x} \right)_{T,P} + T \left(\frac{\partial F}{\partial T} \right)_{x,P},$$

$$\left(\frac{\partial H}{\partial x} \right)_{T,P} = F + T \left(\frac{\partial S}{\partial x} \right)_{T,P} = (aT + b)x + T(-ax) = aTx + bx - Tax = bx$$

$$\implies H(x) = \int bx dx = \frac{1}{2}bx^2.$$

(e) The entropy of the molecule has to decrease when x decreases (we press on the molecule). Thus, the coefficient a has to be negative for $a < 0$, and

$$\left(\frac{\partial H}{\partial x} \right)_{T,P} \ll T \left(\frac{\partial F}{\partial T} \right)_{x,P},$$

$$bx \ll aTx,$$

$$b \ll aT < 0.$$

b is more negative than aT .

15. Gibbs–Helmholtz equation.

From the definition of $G = H - TS$, derive the Gibbs–Helmholtz equation

$$\frac{\partial}{\partial T} \left(\frac{G}{T} \right) = -\frac{H}{T^2},$$

which relates the temperature variation of the Gibbs free energy G to the enthalpy H .

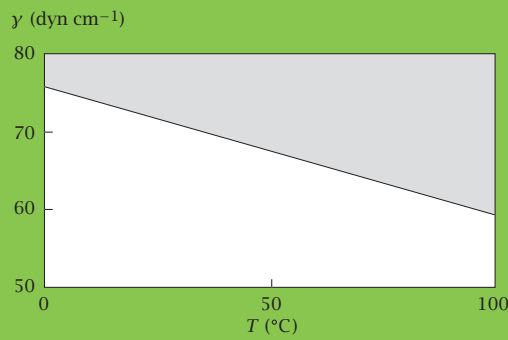
Starting with $G = H - T(\partial G/\partial T)_{p,N}$, and multiplying both sides by $(-1/T^2)$,

$$-\frac{G}{T^2} - \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_{p,N} = -\frac{H}{T^2},$$

$$\frac{\partial}{\partial T} \left(\frac{G}{T} \right) = -\frac{H}{T^2}.$$

16. Surface tension components.

The following figure shows the surface tension of water as a function of temperature:



(Redrawn from data in *CRC Handbook of Chemistry and Physics*, 47th edition, RC Weast, ed., The Chemical Rubber Company, Cleveland, OH, 1962.)

- From the figure, determine the numerical value of $(\partial\gamma/\partial T)_{p,N,A}$, where T = temperature, p = pressure, and a = surface area.
- Find the Maxwell relation for the partial derivative equal to $(\partial\gamma/\partial T)_{p,N,A}$.
- Write an expression for the enthalpic and entropic components of the surface tension γ .
- Combining the results from above, compute the numerical values of the enthalpic and entropic parts of γ at $T = 300$ K, and comment on which component dominates the surface tension.

- (a) From the slope,

$$\frac{\partial\gamma}{\partial T} = -0.15 \text{ dyn cm}^{-1} \text{ deg}^{-1}.$$

- (b) Use Equation (9.5) from Example 9.2 to get the appropriate cross term:

$$\left(\frac{\partial\gamma}{\partial T} \right)_{p,N,A} = - \left(\frac{\partial S}{\partial A} \right).$$

(c)

$$\gamma = \left(\frac{\partial G}{\partial a} \right)_{T,p,N} = \left(\frac{\partial H}{\partial a} \right)_{T,p,N} - T \left(\frac{\partial S}{\partial a} \right)_{T,p,N}.$$

(See Equation (9.20) in Example 9.5 for an equivalent problem.)

(d)

$$\begin{aligned} \text{Entropic part} &= -T \frac{\partial S}{\partial a} = T \frac{\partial \gamma}{\partial T} = 300 \text{ K} \times (-0.15 \text{ dyn cm}^{-1} \text{ deg}^{-1}) \\ &= 45 \text{ dyn cm}^{-1}. \end{aligned}$$

(e) At $T = 300 \text{ K}$, $\gamma \approx 70 \text{ dyn cm}^{-1}$, so the enthalpic part is

$$\frac{\partial H}{\partial a} = \gamma - T \frac{\partial \gamma}{\partial T} = 70 - 45 = 25 \text{ dyn cm}^{-1}.$$

Therefore, the surface tension of water is dominated by entropy. This is because water is a structured liquid.

17. Exploring the quantity F/T .

Sometimes a quantity of interest is the Helmholtz free energy $F(T, V, N)$ divided by T . (For example, this quantity is proportional to the logarithms of equilibrium constants or solubilities.)

(a) Derive a relationship showing that

$$\frac{\partial(F/T)}{\partial T} \propto U.$$

Find the constant of proportionality.

(b) Suppose $F(T)$ depends on temperature in the following way: $F(T) = 2aT^2 + bT$ (so $F/T = 2aT + b$). Find $S(T)$ and $U(T)$.