

## Determining entropy

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The purpose of this note is to collect various ways of determining entropy and entropy changes.

1. **Postulate:** Entropy is postulated to be maximized at equilibrium with respect to small changes in any and every generalized displacement. This makes it easy to figure out equilibrium conditions in the entropy representation because  $dS = 0$  (and  $d^2S < 0$ ):

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \sum_i \frac{\mu_i}{T}dN_i - \frac{V\sigma}{T}d\epsilon - \dots = 0$$

2. **Fundamental definition:**

$$S = -k \sum_i p_i \ln p_i$$

where  $p_i$  is the probability of being in microstate  $i$  (so that  $\sum p_i = 1$ ).

- With  $\Omega$  microstates that are equally probable (the *a priori* equal probability assumption),  $p_i = \frac{1}{\Omega}$  and  $S = k \ln \Omega$ .
- Configurational entropy: if  $N$  items can be arranged into groups of size  $n_1, n_2, n_3, \dots$  (where  $\sum n_j = N$ ), the number of possible microstates is

$$\Omega = \frac{N!}{n_1!n_2!n_3!\dots}$$

Then

$$S = -kN \sum_j x_j \ln x_j$$

where  $x_i = \frac{n_i}{N}$ .

- If there are only two ways in which any one item can be classified (*e.g.*,  $N$  lattice points on which either A or B atoms can sit) and the probability of one of the ways is  $x$ , then

$$S = -kN [x \ln x + (1 - x) \ln(1 - x)]$$

which is the configurational entropy of mixing for an ideal binary solution.

- Entropy is the property of an ensemble and has no microscopic counterpart. Like temperature, it is a non-mechanical variable.

3. **From a partition function:** In the canonical ensemble, the partition function is  $Q$ , the potential of interest is

$$F = F(N, V, E) = -kT \ln Q$$

and as usual

$$dF = -S dT - p dV + \sum_i \mu_i dN_i$$

Therefore

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = kT \left(\frac{\partial \ln Q}{\partial T}\right)_{V,N} + k \ln Q$$

In general, for any partition function  $Z$ , the entropy is

$$S = kT \left(\frac{\partial \ln Z}{\partial T}\right) + k \ln Z$$

where the variables held constant in the partial derivative are the same as those held constant in the system (and in assembling the partition function).

#### 4. Reversible processes:

(a) The closed-system entropy representations

$$dS = \frac{1}{T}dU + \frac{P}{T}dV = \frac{1}{T}dH - \frac{V}{T}dP$$

can be integrated for various reversible processes to give

$$\Delta S = \frac{Q}{T} \quad (\text{isothermal})$$

$$\Delta S = nc_V \ln\left(\frac{T_2}{T_1}\right) \quad (\text{isochoric})$$

$$\Delta S = nc_P \ln\left(\frac{T_2}{T_1}\right) \quad (\text{isobaric})$$

(b) For the potentials that use  $T$  as a natural variable (e.g.,  $F$  and  $G$ ), we have

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

5. **Ideal gas:** Again assuming a closed system, for any process

$$\Delta S = nc_V \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S = nc_P \ln\left(\frac{T_2}{T_1}\right) + nR \ln\left(\frac{P_1}{P_2}\right)$$

6. **Reversible work:** If no heating occurs, there is no change in entropy. Reversible work implies an energy flow with no accompanying entropy flow.

7. **Open systems:** Species entering an open system carry their own entropy.

8. **At a reversible phase transition:** At constant pressure and temperature

$$\Delta S = \frac{\Delta H}{T_{pt}}$$

which matches the earlier result for an isothermal reversible process. Note that the higher-temperature phase always has higher entropy (that's why it's the higher-temperature phase).

9. **Irreversible processes:**

(a) Entropy is a state function, so find a sequence of reversible processes that accomplish the same state, and calculate using those.

(b) From kinetics,

$$\Delta S = \iiint \frac{L|\vec{F}|^2}{T} dt dV$$

where  $\vec{F}$  is a generalized potential gradient (e.g.,  $\vec{F} = -\nabla\mu$ ).

10. **Maxwell and other relations:**

(a) Using a Maxwell relation, we can show that, say,

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

so that

$$\Delta S = -\int V\alpha_V dP$$

which is approximately  $-V\alpha_V\Delta P$  for a condensed phase.

(b) Using the chain rule, we can show that

$$\left(\frac{\partial S}{\partial V}\right)_P = \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P$$

so that

$$\Delta S = \int \frac{nc_P}{TV\alpha_V} dV$$

which may be of interest to somebody.

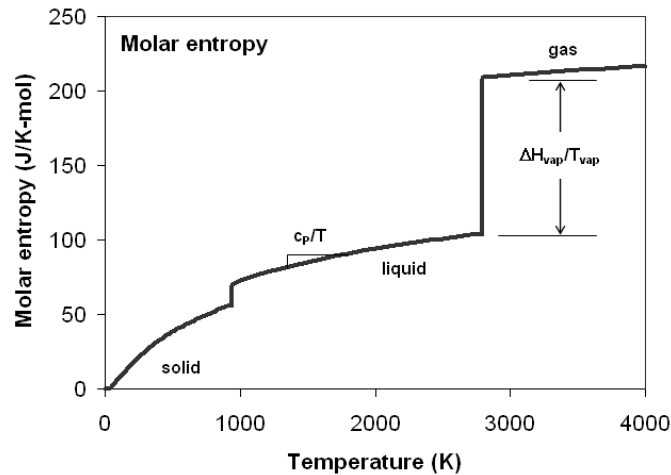
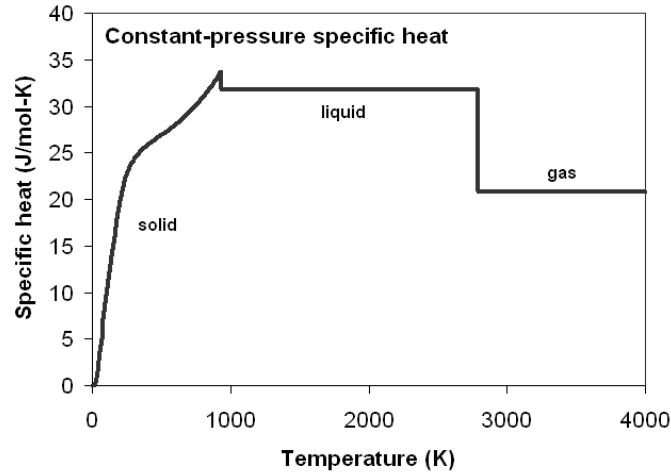
(c) Finally, using the Gibbs-Duham equation

$$-S dT + V dP - \sum N_i d\mu_i - m dh - \dots = 0$$

we can show that

$$S = V \left(\frac{\partial P}{\partial T}\right)_{\mu, h, \dots} = -N \left(\frac{\partial \mu}{\partial T}\right)_{P, h, \dots} = -m \left(\frac{\partial h}{\partial T}\right)_{P, \mu, \dots} = \dots$$

11. **Partial molar entropy:** In a binary system,  $\underline{S} = x_A \bar{S}_A + x_B \bar{S}_B$  (so  $d\underline{S} = \bar{S}_A dx_A + \bar{S}_B dx_B$ ) and  $dx_A = -dx_B$ . Solving for  $\bar{S}_A$ , we have  $\bar{S}_A = \underline{S} - x_B \left( \frac{d\underline{S}}{dx_B} \right)$ , which is the intercept rule.
12. **Typical elemental material:** Shown below is the (roughly) calculated constant-pressure specific heat  $c_p$  and molar entropy  $\underline{S}$  for aluminum ( $T_m = 933 \text{ K}$ ,  $\Delta H_m = 10.7 \text{ kJ mol}^{-1}$ ,  $T_{\text{vap}} = 2792 \text{ K}$ ,  $\Delta H_{\text{vap}} = 294 \text{ kJ mol}^{-1}$ ,  $\Theta_D = 396 \text{ K}$ ).



13. **Forms of entropy:** Anything that can take up energy—like vibrational modes or electrons near the Fermi energy—can contribute to entropy.
- Configurational (solute atoms and/or point defects)
  - Vibrational (typically higher in softer or less-close-packed materials. At high temperatures, BCC may be favored over FCC or HCP)
  - Electronic (very low in insulators, low to medium for semiconductors and metals, high for ionic conductors)