Unit 2 Summary

You need to know the Boltzmann equation in terms of probability and fractional occupancy in a two level system. In general, the Boltzmann equation gives the probability, P_j, that a randomly chosen system (from an ensemble of systems in thermal contact) will be in state j with energy $E_j(N,V)$:

$$P_j(N,V,T) = \frac{a_j}{A} = \frac{e^{-E_j(N,V)/k_B T}}{Q(N,V,T)}$$

The system partition function is $Q(N,V,\beta) = \sum_i e^{-\beta E_i(N,V)} = \frac{[q(v,\beta)]^N}{N!}$ for

indistinguishable particles.

For the two-level system:

$$\frac{N_2}{N_1} = e^{-(E_2 - E_1)/k_B T}, \quad N_1 = N\frac{1}{1 + e^{-\Delta E/k_B T}}, \quad N_2 = N\frac{1}{1 + e^{+\Delta E/k_B T}}$$

You should be able to obtain partition functions for simple energy level systems.

The Boltzmann equation seeks to find the maximum number of configurations. For a system with large N, there is a configuration with so great a weight that is overwhelms the rest. The system will almost always be found in it, and it will determine the properties of the system. The Boltzmann equation gives the probability of realizing this configuration as a function of energy and temperature.

Energy can be evaluated form the partition function:

For the system:
$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

For the atom/molecule:
$$\langle \varepsilon \rangle = -\left(\frac{\partial \ln q}{\partial \beta}\right)_{N,V} = k_B T^2 \left(\frac{\partial \ln q}{\partial T}\right)_{N,V}$$

$$\langle E \rangle = N \langle \varepsilon \rangle, \text{ and for 1 mol: } \langle \overline{E} \rangle = N_A \langle \varepsilon \rangle = \overline{U}$$

and so we see that $\overline{U} = N_A k_B T^2 \left(\dfrac{\partial \ln q}{\partial T} \right)_V$

Heat capacity and pressure can also be evaluated from the partition function:

$$C_v = \left(\frac{\partial U}{\partial T} \right)_{N,V} \quad \text{and} \quad \langle P \rangle = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{N,\beta}$$

You should be able to calculate any of these properties for any partition function I give you. Here follows some results for a diatomic molecule. You should understand (and derive completely) how these results were obtained.

The translational partition function (3D): $\qquad q_{trans}(V,T) = \left(\dfrac{2\pi M k_B T}{h^2} \right)^{3/2} V$

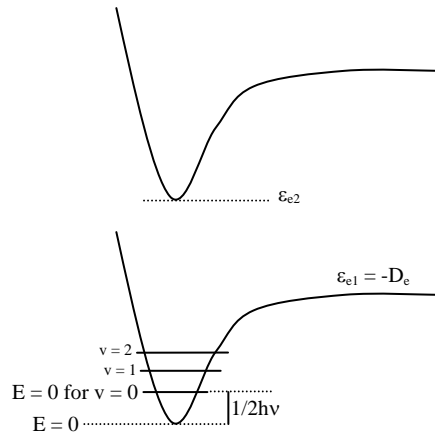The rotational partition function (large T): $\qquad q_{rot}(T) = \dfrac{8\pi^2 I k_B T}{h^2}$

The vibrational partition function: $\qquad q_{vib}(T) = \dfrac{e^{-\Theta_{vib}/2T}}{1 - e^{-\Theta_{vib}/T}}$

The vibrational partition function depends on how we define the zero of energy. If we define it as the bottom of the internuclear potential, we obtain the above expression. However if we define zero as the v = 0 state, then we obtain the following expression:

$$q_{vib}(T) = \frac{1}{1 - e^{-\Theta_{vib}/T}}$$

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The expression for the rotational partition function above works for high temperatures. Room temperature measurements have to calculated numerically using the following equation.

$$q_{rot}(T) = 1 + 3e^{-2B/k_BT} + 5e^{-6B/k_BT} + \ldots$$

From these partition functions the following can be obtained.

	$\overline{U}$	$\overline{C}_V$
Translational	$\dfrac{3}{2}RT$	$\dfrac{3}{2}R$
Rotational	RT	R
Vibrational	$R\left(\dfrac{\Theta_{vib}}{2} + \dfrac{\Theta_{vib}}{e^{\Theta_{vib}/T} - 1}\right)$	$R\left(\dfrac{\Theta_{vib}}{T}\right)^2 \dfrac{e^{-\Theta_{vib}/T}}{\left(1 - e^{-\Theta_{vib}/T}\right)^2}$

Total internal energy is the sum of the individual internal energies and total heat capacity is the sum of the individual heat capacities. Note, we have ignored the electronic contribution.

Note $q(V,T) = q_{trans}q_{rot}q_{vib}q_{elec}$ and $\varepsilon_{total} = \varepsilon_{trans} + \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{elec}$

WORK, ENERGY & HEAT

Work is the transfer of energy due to unbalanced forces: $w = -P_{ext}\Delta V$

If P_{ext} is not constant during the process: $w = -\int_{V_i}^{V_f} P_{ext}dV$

For a reversible process (compression or expansion of an ideal gas):

$$w = -nRT \ln\frac{V_2}{V_1}$$

The first law of thermodynamics: $\boxed{\begin{array}{l} dU = \delta q + \delta w \\ \Delta U = q + w \end{array}}$ Path & state functions: know the difference.

Some important processes:

ISOLATED SYSTEM: $q = 0, \quad w = 0, \quad \Delta U = 0$

ISOTHERMAL (no change in T): $\Delta U = 0$
$\Delta T = 0$

$$w_{rev} = -q_{rev} = -nRT \ln\frac{V_2}{V_1}$$

ADIABATIC (no change in q): $q = 0$

$$\Delta U = w_{rev} = \int_{T_1}^{T_2} C_V(T)dT$$

PRESSURE-VOLUME WORK: $\Delta U = q_V$ (constant volume)

$H = U + PV$
$\Delta H = \Delta U + P\Delta V \left.\right\}$ constant pressure
$q_P = \Delta H$

The temperature of a gas decreases in a reversible adiabatic expansion:

$$\left(\frac{T_2}{T_1}\right)^{3/2} = \frac{V_1}{V_2} \quad \text{(Know the derivation)}$$

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ENTHAPLY

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At constant pressure: $\Delta H = \Delta U + P\Delta V$, and $q_P = \Delta H$

To calculate the enthalpy from T = 0K to T = T, must take into account any phase transitions.

$$H(T) - H(0) = \int_0^{T_{fus}} C_P^S(T)dT + \Delta_{fus}H + \int_{T_{fus}}^{T} C_P^L(T)dT \text{, etc. In other words } \Delta H = \int C_P dT$$

Note also that $C_P = \dfrac{\Delta H}{\Delta T}$, and $C_P - C_V = nR$

Make sure you know how to calculate enthalpy changes for chemical reactions. You can use Hess's law and enthalpies of formation to calculate enthalpies of reaction. Know how to calculate enthalpy changes at different temperatures using the following equation:

$$\Delta H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2} \left[C_P(products) - C_P(react's)\right]$$

ENTROPY

Entropy (state function): $dS = \dfrac{\delta q_{rev}}{T}$

$dS = 0$ Equilibrium (reversible process)

$dS > 0$ Spontaneous process in isolated system

Know the Second Law.

Isothermal expansion: $\quad \Delta \bar{S} = R \ln \dfrac{V_2}{V_1}$, For mixing of two gases:

$$\Delta_{mix}\bar{S} = -R \sum_{j=1}^{N} y_i \ln y_i \text{ (Learn the derivation)}$$

The Third Law: Every substance has finite positive entropy, but at 0 K the entropy may become 0, and does so in the case of a perfectly crystalline substance.

Determining absolute entropies from calorimetric data:

$$S(T) = \int_0^{T_{fus}} \frac{C_P^S(T)dT}{T} + \frac{\Delta_{fus}H}{T_{fus}} + \int_{T_{fus}}^{T_{vap}} \frac{C_P^L(T)dT}{T} + \frac{\Delta_{vap}H}{T_{vap}} + \int_{T_{vap}}^{T} \frac{C_P^g(T)dT}{T}$$

These entropies are usually called "calorimetric entropies." Note we have assumed the Third Law holds true for calorimetric entropies.

Statistical Entropy: $\quad S = k_B \ln W$

From partition functions:

$$S = k_B \ln Q + k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} = Nk_B + Nk_B \ln\left[\frac{q(V,T)}{N} \right] + Nk_B T \left(\frac{\partial \ln q}{\partial T} \right)_V$$

Note that the above expression relates entropy to the system partition function (Q) and the molecular partition function (q). Make sure you know how to go from the expression for system Q to molecular q, using Stirling's approximation (lnN! = NlnN – N).

The molar entropy of an ideal monoatomic gas: $\bar{S} = \dfrac{5}{2}R + R\ln\left[\left(\dfrac{2\pi m k_B T}{h^2} \right)^{3/2} \dfrac{\bar{V}g_{e1}}{N_A} \right]$

The molar entropy of a diatomic gas is given by:

$$\frac{\bar{S}}{R} = ln\left[\left(\frac{2\pi Mk_BT}{h^2}\right)^{3/2}\frac{\bar{V}e^{5/2}}{N_A}\right] + ln\frac{Te}{2\Theta_{rot}} - ln\left(1 - e^{-\Theta_{vib}/T}\right) + \frac{\Theta_{vib}/T}{e^{\Theta_{vib}/T} - 1} + ln\,g_{el}$$

You should be able to derive entropy expressions using simple partition functions. You should be able to determine entropies of monoatomic and diatomic molecules from spectroscopic parameters. The entropies are generally called "statistical entropies."

We have assumed the Third Law holds perfectly when calculating calorimetric entropies, i.e. $\Delta S = 0$ at $T = 0$ K. Spectroscopic entropies are therefore more accurate. Realize that at 0 K some molecules (usually those possessing small dipoles) may get "locked" into two or more possible degenerate states, e.g. CO and linear NNO, W = 2; CH_3D, W = 4. You should be able to calculate residual entropies, and add the values to the calorimetric values to get entropies in closer agreement to statistical ones.

PREDICTING SPONTANEOUS PROCESSES

Helmholtz Energy: $\Delta A = \Delta U - T\Delta S \leq 0$ **For constant T and V**

                                      $\Delta A < 0$ Spontaneous (irreversible)

                                      $\Delta A > 0$ Not spontaneous

                                      $\Delta A = 0$ Equilibrium

Gibbs Energy: $\Delta G = \Delta H - T\Delta S$ **For constant T and P**

                                      $\Delta G < 0$ Spontaneous (irreversible)

                                      $\Delta G > 0$ Not spontaneous

                                      $\Delta G = 0$ Equilibrium

Be aware that the Maxwell relations allow us to derive some important thermodynamic equations. Two important ones are the temperature and the pressure dependency of the Gibbs energy.

$\left(\dfrac{\partial G}{\partial T}\right)_P = -S$ Which gives: $\left(\dfrac{\partial G/T}{\partial T}\right)_P = -\dfrac{H}{T^2}$ GIBBS-HELMHOLTZ EQUATION

$\left(\dfrac{\partial G}{\partial P}\right)_T = V$ Which gives: $\Delta\bar{G} = RT\,ln\dfrac{P_2}{P_1}$

Using the above we find $-\left(\dfrac{\partial S}{\partial P}\right)_T = \left(\dfrac{\partial V}{\partial T}\right)_P$

Other important ones are: $\left(\dfrac{\partial A}{\partial V}\right)_T = -P$ and $\left(\dfrac{\partial A}{\partial T}\right)_V = -S$ so that using cross

derivatives, we find that $\left(\dfrac{\partial P}{\partial T}\right)_V = \left(\dfrac{\partial S}{\partial V}\right)_T$

At P_1 = 1 bar $\overline{G}(T,P) = \overline{G}^o(T) + RT\,ln\,P$, where $\overline{G}^o(T)$ = standard molar Gibbs energy.

For non-ideal gases $\overline{G}(T,P) = \overline{G}^o(T) + RT\,ln\,\dfrac{f(P,T)}{f^o}$, where f(P,T) = fugacity of

gas.

Using the virial equation for non-ideality:
$$\dfrac{f(P,T)}{f^o} = \dfrac{P}{P^o}\,exp\left[B_{2P}(T)P + B_{3P}(T)P^2 + ...\right]$$

Note, the fugacity coefficient $\gamma = \dfrac{f}{P}$, and $ln\,\gamma = \displaystyle\int_0^P \dfrac{Z-1}{P}\,dP$, where $Z = \dfrac{P\overline{V}}{RT}$

(Z = compressibility factor)