A "generalized brightness theorem" is derived that describes the thermodynamic limitations of the fluorescent planar concentrator. The maximum brightness concentration ratio allowed by thermodynamics is \( \exp \left( \frac{h \Delta \nu}{kT} \right) \) where \( \Delta \nu \) is the Stokes shift.

The diffuse nature of sunlight has been an obstacle to the widespread application of solar energy conversion technologies. A means of addressing this problem is the fluorescent planar concentrator, which relies on the principle of total internal reflection to concentrate the radiant energy. This poses an interesting thermodynamic question since the light concentration must come at the expense of an entropy increase somewhere else in the system.

Figure 1 shows a diagram of the fluorescent planar concentrator, with the incident light field \( I_1 \) and the concentrated light field \( I_2 \). According to statistical mechanics \( \Delta S \) the entropy change associated with the loss of a photon from the incident Bose field is

\[
\Delta S_1 = -k \log \left( 1 + \frac{8 \pi n^2 \nu^2}{c^2 B_1} \right),
\]

where \( n \) is the index of refraction, \( \nu \) the frequency, and \( B_1 \) the brightness of the incident field in photons per unit area, per unit bandwidth, per unit time, and per 4\( \pi \) solid angle. The entropy increase in the concentrated field due to the fluorescent emission of one photon is

\[
\Delta S_2 = k \log \left( 1 + \frac{8 \pi n^2 \nu^2}{c^2 B_2} \right) + \frac{h(\nu_1 - \nu_2)}{T},
\]

where the additional term is due to the thermal dissipation of the Stokes shift \( \nu_1 - \nu_2 \) at the ambient temperature \( T \). According to the second law of thermodynamics, \( \Delta S_1 + \Delta S_2 \geq 0 \), therefore,

\[
K \log \left( 1 + \frac{8 \pi n^2 \nu^2}{c^2 B_1} \right) / \left( 1 + \frac{8 \pi n^2 \nu^2}{c^2 B_2} \right) \leq \frac{h(\nu_1 - \nu_2)}{T}.
\]

Under typical terrestrial conditions this may be approximated as

\[
C = \frac{B_2}{B_1} \leq \frac{\nu_2^2}{\nu_1^2} \exp \left( \frac{h(\nu_1 - \nu_2)}{kT} \right).
\]

The maximum concentration ratio \( C \) in a fluorescent planar concentrator depends sensitively on the Stokes shift. Equations (3) and (4) may be regarded as a generalization of the well-known "brightness theorem" of optics to the case of inelastic processes, \( \nu_1 \neq \nu_2 \).

In this article we develop a theory of the fluorescent planar concentrator based on thermodynamics. Therefore it will automatically be consistent with Eqs. (3) and (4).

Consider an ensemble of fluorescent molecules that are optically excited out of equilibrium with the ambient temperature \( T \). By virtue of the mean excitation, the absorption of one additional photon will be accompanied by an increase in free energy of

\[
\mu = \Delta F = h \nu - T \Delta S,
\]

where \( \Delta S \) is the change in entropy of the molecule. For equilibrium of the molecular electronic degrees of freedom with the radiation field, the entropy change \( \Delta S \) in Eq. (5) should exactly balance the entropy change \( \Delta S \) in Eq. (1):

\[
K \log \left( 1 + \frac{8 \pi n^2 \nu^2}{c^2 B} \right) = \frac{h \nu - \mu}{T}.
\]

Therefore, the brightness of a radiation field that is in equilibrium with the electronic degrees of freedom of the molecule is

\[
B(\nu, \mu, T) = \frac{8 \pi n^2 \nu^2}{c^2} \left( \frac{e^{(h \nu - \mu)/kT} - 1}{1} \right).
\]

It is implicit that there is fast thermal equilibration among the vibrational substates of the electronically excited state. For the situation where \( \mu = 0 \), i.e., no electronic excitation, Eq. (7) reduces to the ambient temperature Planck distribution as it should.

Consider the radiative equilibrium from the viewpoint of an individual molecule. Its net rate of up transition should exactly balance its rate of spontaneous emission \( F(\nu, \mu, T) \) at each frequency. This is the well-known principle of detailed balance:

\[
F(\nu, \mu, T) = \sigma(\nu, \mu, T)B(\nu, \mu, T),
\]

where \( \sigma(\nu, \mu, T) \) is the net absorption cross section.

Now suppose that the electronic excitation is produced by some means other than the radiation field described by Eq. (7). For example, the electronic excitation may be produced by a different optical spectrum or by electron impact or chemiactivation. Provided there is fast thermal equilibration among the vibrational substates of the electronically excited state, there will be no memory of the excitation process and \( \mu \) will be determined only by the net rate of upward electronic transitions. Therefore, the fluorescent spectrum will be given by Eq. (8) irrespective of the excitation mechanism.

This model of the fluorescent spectrum was first developed by E. H. Kennard and has been independently rediscovered several times in the past 60 years. For example, when applied to semiconductors, Eq. (8) is known as the van Roosbroeck-Schockley relation. We have closely followed the approach given by Ross.

The chemical potential \( \mu \) will be determined by the steady-state balance of up and down transitions. Let the light intensity be defined as

\[
I(\nu) = \int B(\nu) \frac{d\Omega}{4\pi}.
\]

The up transitions are produced by absorption from the in-
incident sunlight intensity $I_1$, as well as self-absorption of the trapped concentrated light field $I_2$:

$$\int \sigma(v) I_1(v) dv + \int \sigma(v) I_2(v) dv = \int \frac{\sigma(v)}{Q e^{(h\nu-\mu)/KT}} \frac{8\pi n^2 \nu^2}{c^2} d\nu \left( \frac{\Omega_1}{4\pi} + \frac{\Omega_2}{4\pi} \right).$$

(9)

The rate of downward spontaneous transitions that appears on the right-hand side of Eq. (9) is divided by the quantum efficiency $Q$ to give the total downward transition rate. Solid angle $\Omega_1$ is the escape cone and $\Omega_2$ is the totally internally reflected solid angle. Equation (9) should be solved to determine $\mu$ in steady state. Under terrestrial conditions ($h\nu-\mu$) $\gg KT$, in which case the 1 may be dropped from the denominator and we are justified in regarding the absorption cross section as independent of $\mu$. This is because the excited-state population will be small and the absorption will be predominantly from the ground state.

Let us now consider the problem of the spatial growth of the concentrated intensity $I_2(\nu, x)$, where $x$ is the position measured from one edge of the collector:

$$\frac{dI_2(\nu, x)}{dx} = -N\sigma(\nu) I_2 + \frac{N\sigma(\nu)}{e^{(h\nu-\mu)/KT}} \frac{8\pi n^2 \nu^2 \Omega_2}{4\pi c^2},$$

(10)

where the first term on the right-hand side is the self-absorption of the fluorescence, the second term is one-half the trapped fluorescent emission (since we are considering only sorption of the fluorescence, the second term is one-half the total absorption contribution to the chemical potential in Eq. (9)). Dropping the self-absorption term in Eq. (9) decouples Eqs. (9) and (10). Then the chemical potential is uniquely determined and is independent of position. For a given Stokes shift of a fluorescent molecule, the geometrical concentration ratio to be far below the constraints of inequality (4). In practice, efficient operation requires that the concentration ratio be designed within the constraints of inequality (4). It is also clear from Eq. (11) that the problem cannot be solved simply by finding a molecule where the absorption and emission bands do not overlap. The two are inextricably linked by Eq. (8) in such a way that the thermodynamic limit cannot be exceeded. For very high concentration ratios, materials with very large Stokes shifts must be found.