CBE 60553, Fall 2017, Homework 1

Problem 1: Choose your path wisely

A particular system has the equation of state $U = \frac{5}{2}PV + C$, where C is an undetermined constant.

1. The system starts at state A, in which $P = 0.2\ MPa$ and $V = 0.01\ m^3$. It is taken quasistatically along the path shown in the figure ($A \rightarrow B$, $B \rightarrow C$, $C \rightarrow A$). Calculate the heat transferred from the surroundings, q, and the work done on the system, w, for each step along the path.

i) $A \rightarrow B$

$$
\begin{aligned}
U_{AB} = U_B - U_A = \frac{5}{2}(P_B V_B - P_A V_A) = 10000\ J \\
W_{AB} = -\int_{V_A}^{V_B} P dV = -P(V_B - V_A) = -4000\ J \\
\therefore\ Q_{AB} = U_{AB} - W_{AB} = 14000\ J
\end{aligned}
$$

ii) $B \rightarrow C$

Need pressure as a function of volume along this path. From the figure, the relationship is linear and given by

$$P(V) = -15 \times 10^6 V + 0.65 \times 10^6$$

Integrate to find the work

$$W_{BC} = -\int_{V_B}^{V_C} P dV = -\left[\frac{-15 \times 10^6 V^2}{2} + 0.65 \times 10^6 V\right]_{V_B}^{V_C} = 7000\ J$$

From our expression for U

$$
\begin{aligned}
U_{BC} = U_C - U_B = \frac{5}{2}(P_C V_C - P_B V_B) = -2500\ J \\
\therefore\ Q_{BC} = U_{BC} - W_{BC} = -9500\ J
\end{aligned}
$$

iii) $C \rightarrow A$

$$U_{CA} = U_A - U_C = \frac{5}{2}(P_A V_A - P_C V_C) = -7500\ J$$

Since volume is constant

$$
\begin{aligned}
W_{CA} = -\int_{V_C}^{V_A} P dV = 0 \\
\therefore\ Q_{CA} = U_{CA} - W_{CA} = -7500\ J
\end{aligned}
$$

2. Calculate q and w for a quasistatic process starting at A and ending at B along the path $P = a + b(V - c)^2$, where $a = 0.1\ MPa$, $b = 1 \times 10^3\ MPa \cdot m^{-6}$, and $c = 0.02\ m^3$.

$A \rightarrow B$

Along the Parabola

$$P = 10^5 + 10^9 \times (V - 0.02)^2$$

the work can be found by integration

$$W_{AB} = -\int_{V_A}^{V_B} PdV = -\int_{V_A}^{V_B} \left[10^5 + 10^9 \times (V - 0.02)^2\right] dV = -\left[10^5 V + \frac{10^9}{3}(V - 0.02)^3\right]_{0.01}^{0.03} = -2666.67\ J$$

Since

$$U_{AB} = 10000\ J$$

then

$$Q_{AB} = U_{AB} - W_{AB} = 10000\ J - (-2666.67\ J) = 12666.67\ J$$

3. The system exchanges both heat and work with its surroundings along the paths above. An /adiabat/ is a particular quasistatic path along which work is done but no heat is transferred. Find the form of the adiabats $P = P(V)$ for the system described by $U = \frac{5}{2}PV + C$. (Hint: If $\bar{d}\, q_{\text{qs}} = 0$, then $dU = \bar{d}\, w_{\text{qs}} = -PdV$. What else does dU equal?)

For an adiabatic system,

$$dU = dQ - PdV = -PdV$$

and we can also write

$$\begin{gathered} dU = \frac{\partial U}{\partial V}\bigg|_P dV + \frac{\partial U}{\partial P}\bigg|_V dP = 2.5PdV + 2.5VdP = -PdV \\ \frac{7}{V}dV = -\frac{5}{P}dP \\ lnV^7\big|_{V_0}^{V} = -lnP^5\big|_{P_0}^{P} \\ lnP^5V^7 = C'\ (C' = const) \\ P^5V^7 = C\ (C = const) \end{gathered}$$

Problem 2: Is it fundamental enough?

The following ten equations are purported to be fundamental equations for various thermodynamic systems. Five, however, are inconsisent with the basic postulates of a fundamental equation and are thus unphysical. For each, plot the relationship between S and U and identify the five that are unacceptable. v_0 , θ, and R are all positive constants and, in the case of fractional exponents, the real positive root is to be implied.

$(1)\ S = \left(\frac{R^2}{v_0\theta}\right)^{1/3}(NVU)^{1/3} \qquad (2)\ S = \left(\frac{R}{\theta^2}\right)^{1/3}\left(\frac{NU}{V}\right)^{2/3}$

$(3)\ S = \left(\frac{R}{\theta}\right)^{1/2}\left(NU + \frac{R\theta V^2}{v_0^2}\right)^{1/2} \qquad (4)\ S = \left(\frac{R^2\theta}{v_0^3}\right)\frac{V^3}{NU}$

$(5)\ S = \left(\frac{R^3}{v_0\theta^2}\right)^{1/5}\left(N^2U^2V\right)^{1/5} \qquad (6)\ S = NR\ln\left(\frac{UV}{N^2R\theta v_0}\right)$

$(7)\ S = \left(\frac{NRU}{\theta}\right)^{1/2}\exp\left(-\frac{V^2}{2N^2v_0^2}\right) \qquad (8)\ S = \left(\frac{NRU}{\theta}\right)^{1/2}\exp\left(-\frac{UV}{NR\theta v_0}\right)$

$(9)\ U = \left(\frac{NR\theta V}{v_0}\right)\left(1 + \frac{S}{NR}\right)\exp(-S/NR) \qquad (10)\ U = \left(\frac{v_0\theta}{R}\right)\frac{S^2}{V}\exp(S/NR)$

There are three postulates we are testing for

$(i)\ S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N)$: Postulate 3

$(ii)\ \frac{\partial S}{\partial U} > 0$: Postulate 2

$(iii)\ \frac{\partial U}{\partial S} = 0,\ as\ S \to 0$: Postulate 4

We assume $v_0 = 1$, $R = 1$, $\theta = 1$, and N and V are constants.

$(1)\ S = \left(\frac{R^2}{v_0\theta}\right)^{1/3}(NVU)^{1/3} = (NVU)^{1/3}$

$(i)\ S(\lambda U, \lambda V, \lambda N) = (\lambda^3 NVU)^{1/3} = \lambda \cdot NVU = \lambda S(U, V, N)$

$(ii)\ \frac{\partial S}{\partial U} > 0$

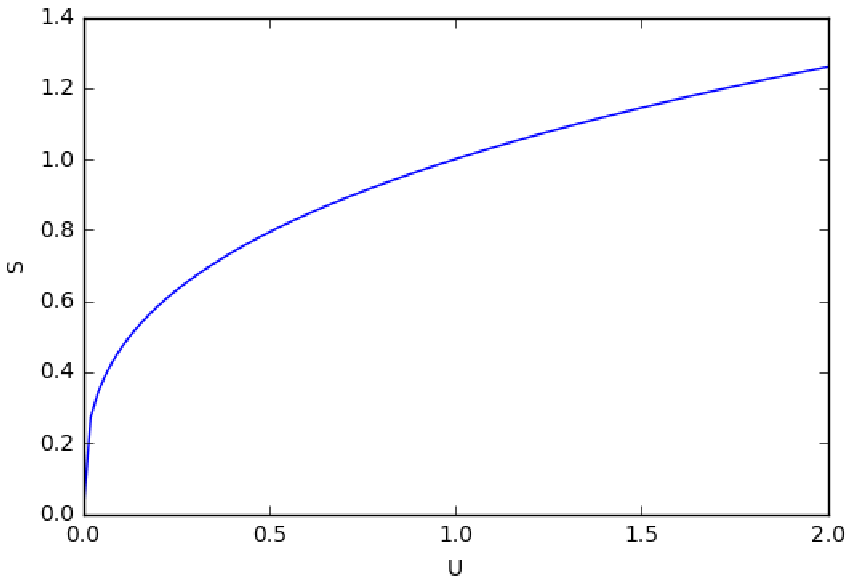
$(iii)\ \frac{\partial U}{\partial S} = 0,\ as\ S \to 0$

$\therefore (1)$ is acceptable.

In [91]:
```
import matplotlib.pyplot as plt
import numpy as np

U = np.linspace(0,2,100)
S = []
for u in U:
    s = u **(1./3)  # assume N = 1 and V = 1
    S.append(s)

plt.plot(U, S,'-')
plt.xlabel('U')
plt.ylabel('S')
plt.show()
```



(2) $S = \left(\frac{R}{\theta^2}\right)^{1/3} \left(\frac{NU}{V}\right)^{2/3} = \left(\frac{NU}{V}\right)^{2/3}$

$(i)\ S(\lambda U, \lambda V, \lambda N) = \left(\lambda \frac{NU}{V}\right)^{2/3} = \lambda^{2/3} \left(\frac{NU}{V}\right)^{2/3} \neq \lambda S(U, V, N)$

$(ii)\ \frac{\partial S}{\partial U} > 0$

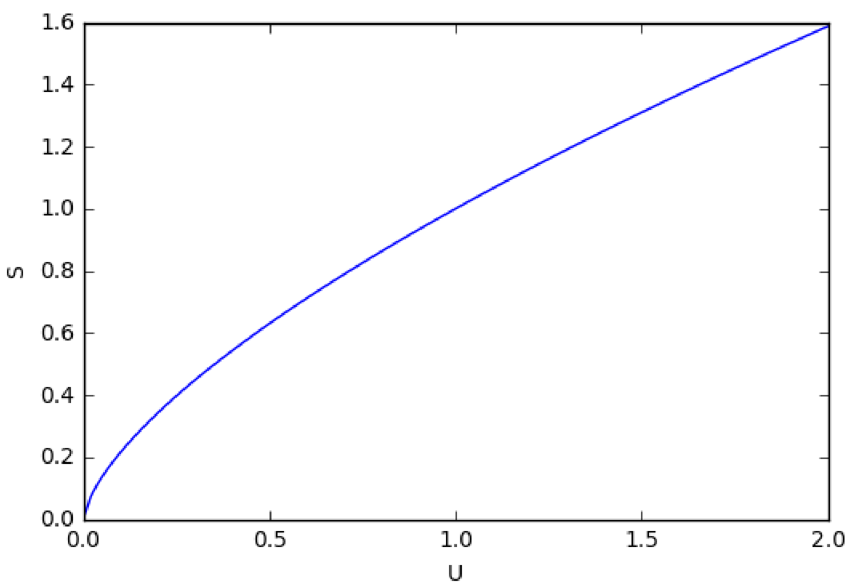
$(iii)\ \frac{\partial U}{\partial S} = 0,\ as\ S \rightarrow 0$

$\therefore$ (2) is not acceptable.

In [90]:
```
import matplotlib.pyplot as plt
import numpy as np

U = np.linspace(0,2,100)
S = []
for u in U:
    s = u **(2./3)  # assume N = 1 and V = 1
    S.append(s)

plt.plot(U, S,'-')
plt.xlabel('U')
plt.ylabel('S')
plt.show()
```



(3) $S = \left(\frac{R}{\theta}\right)^{1/2} \left(NU + \frac{R\theta V^2}{v_0^2}\right)^{1/2} = \left(NU + V^2\right)^{1/2}$

$(i)\ S(\lambda U, \lambda V, \lambda N) = \left(\lambda^2 NU + \lambda^2 V^2\right)^{1/2} = \lambda\left(NU + V^2\right)^{1/2} = \lambda S(U, V, N)$

$(ii)\ \frac{\partial S}{\partial U} > 0$

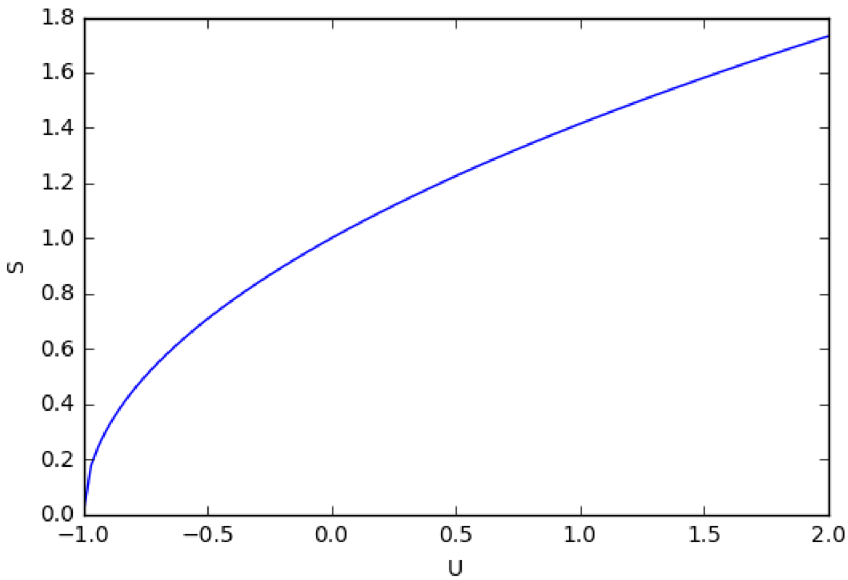
$(iii)\ \frac{\partial U}{\partial S} = 0,\ as\ S \rightarrow 0$

$\therefore$ (3) is acceptable.

In [89]:
```
import matplotlib.pyplot as plt
import numpy as np

U = np.linspace(-1,2,100)
S = []
for u in U:
    s = (u + 1**2)**(1./2)  # assume N = 1 and V = 1
    S.append(s)

plt.plot(U, S,'-')
plt.xlabel('U')
plt.ylabel('S')
plt.show()
```



$(4)\ S = \left(\frac{R^2\theta}{v_0^3}\right)\frac{V^3}{NU} = \frac{V^3}{NU}$

$(i)\ S(\lambda U, \lambda V, \lambda N) = \lambda\frac{V^3}{NU} = \lambda S(U, V, N)$

$(ii)\ \frac{\partial S}{\partial U} < 0$

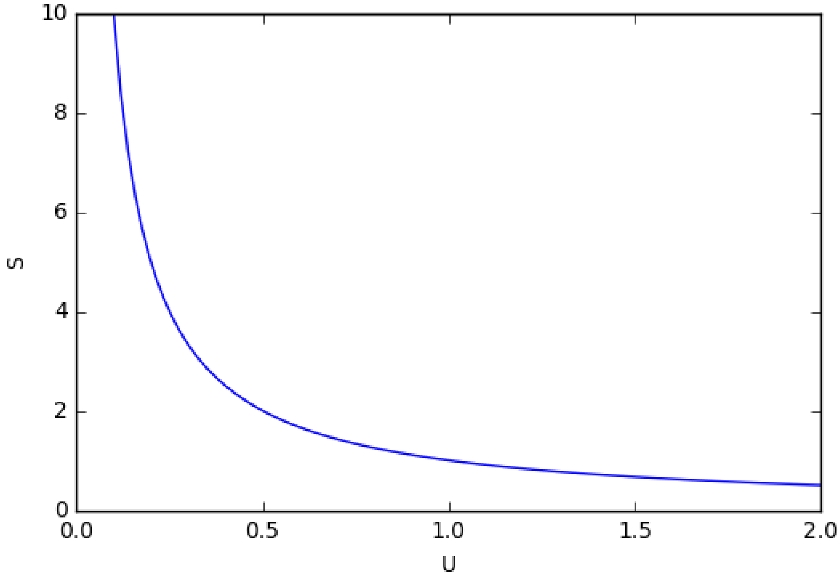
$(iii)\ \frac{\partial U}{\partial S} \neq 0,\ as\ S \to 0$

$\therefore (4)$ is not acceptable.

In [61]:
```python
import matplotlib.pyplot as plt
import numpy as np

U = np.linspace(0.1,2,100)
S = []
for u in U:
    s = (1**3) / (1 * u)  # assume N = 1 and V = 1
    S.append(s)

plt.plot(U, S,'-')
plt.xlabel('U')
plt.ylabel('S')
plt.show()
```



$(5)\ S = \left(\frac{R^3}{v_0\theta^2}\right)^{1/5}\left(N^2U^2V\right)^{1/5} = \left(N^2U^2V\right)^{1/5}$

$(i)\ S(\lambda U, \lambda V, \lambda N) = \lambda\left(N^2U^2V\right)^{1/5} = \lambda S(U, V, N)$

$(ii)\ \frac{\partial S}{\partial U} > 0$

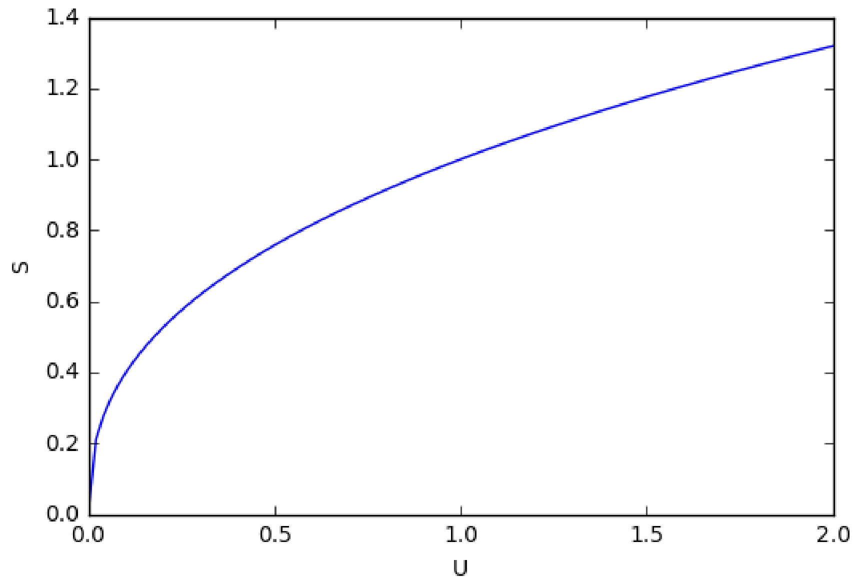
$(iii)\ \frac{\partial U}{\partial S} = 0,\ as\ S \to 0$

$\therefore (5)$ is acceptable.

In [51]:
```
import matplotlib.pyplot as plt
import numpy as np

U = np.linspace(0,2,100)
S = []
for u in U:
    s = (u**2)**(1./5)  # assume N = 1 and V = 1
    S.append(s)

plt.plot(U, S,'-')
plt.xlabel('U')
plt.ylabel('S')
plt.show()
```



$(6)\ S = NR\ln\left(\frac{UV}{N^2R\theta v_0}\right) = N\ln\left(\frac{UV}{N^2}\right)$

$(i)\ S(\lambda U, \lambda V, \lambda N) = \lambda N\ln\left(\frac{UV}{N^2}\right) = \lambda S(U, V, N)$

$(ii)\ \frac{\partial S}{\partial U} > 0$

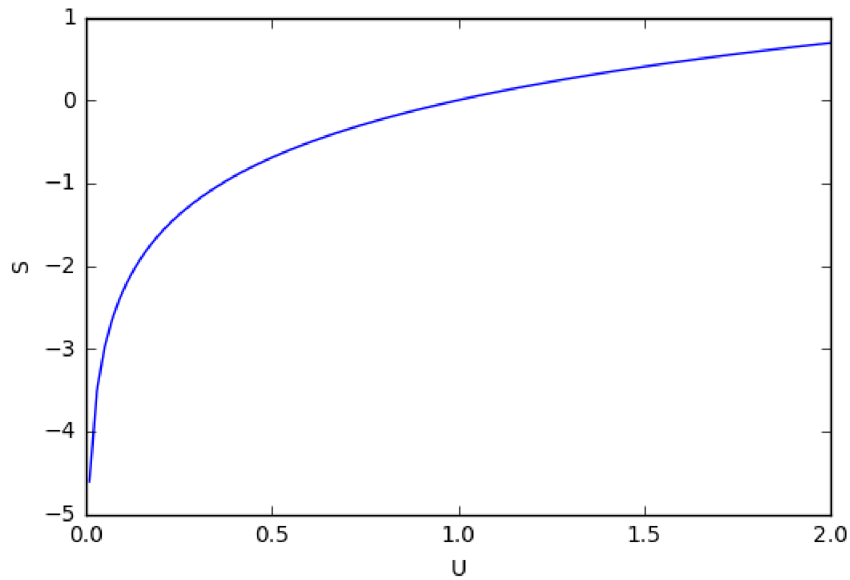
$(iii)\ \frac{\partial U}{\partial S} \neq 0,\ as\ S \to 0$

$\therefore (6)$ is not acceptable.

In [58]:
```
import matplotlib.pyplot as plt
import numpy as np

U = np.linspace(0.01,2,100)
S = []
for u in U:
    s = np.log(u)  # assume N = 1 and V = 1
    S.append(s)

plt.plot(U, S,'-')
plt.xlabel('U')
plt.ylabel('S')
plt.show()
```



$(7)\ S = \left(\frac{NRU}{\theta}\right)^{1/2} \exp\left(-\frac{V^2}{2N^2v_0^2}\right) = (NU)^{1/2}\exp\left(-\frac{V^2}{2N^2}\right)$

$(i)\ S(\lambda U, \lambda V, \lambda N) = \lambda (NU)^{1/2}\exp\left(-\frac{V^2}{2N^2}\right) = \lambda S(U,V,N)$

$(ii)\ \frac{\partial S}{\partial U} > 0$

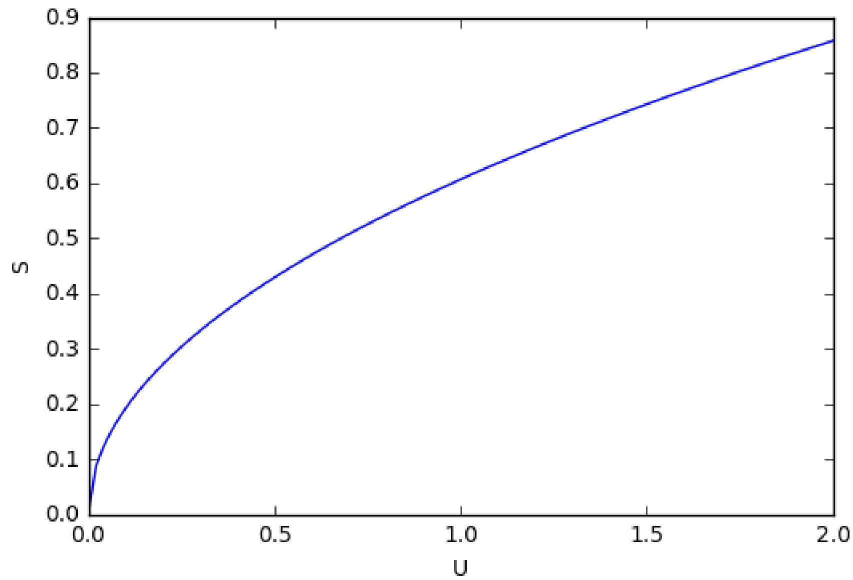
$(iii)\ \frac{\partial U}{\partial S} = 0,\ as\ S \to 0$

$\therefore$ (7) is acceptable.

In [63]:
```
import matplotlib.pyplot as plt
import numpy as np

U = np.linspace(0,2,100)
S = []
for u in U:
    s = (u**(0.5)) * np.exp(-0.5) # assume N = 1 and V = 1
    S.append(s)

plt.plot(U, S,'-')
plt.xlabel('U')
plt.ylabel('S')
plt.show()
```



(8) $S = \left(\frac{NRU}{\theta}\right)^{1/2} \exp\left(-\frac{UV}{NR\theta v_0}\right) = (NU)^{1/2} \exp\left(-\frac{UV}{N}\right)$

(i) $S(\lambda U, \lambda V, \lambda N) = \lambda (NU)^{1/2} \exp\left(-\lambda \frac{UV}{N}\right) \neq \lambda S(U, V, N)$

(ii) $\frac{\partial S}{\partial U}$ is not monotonically increasing.

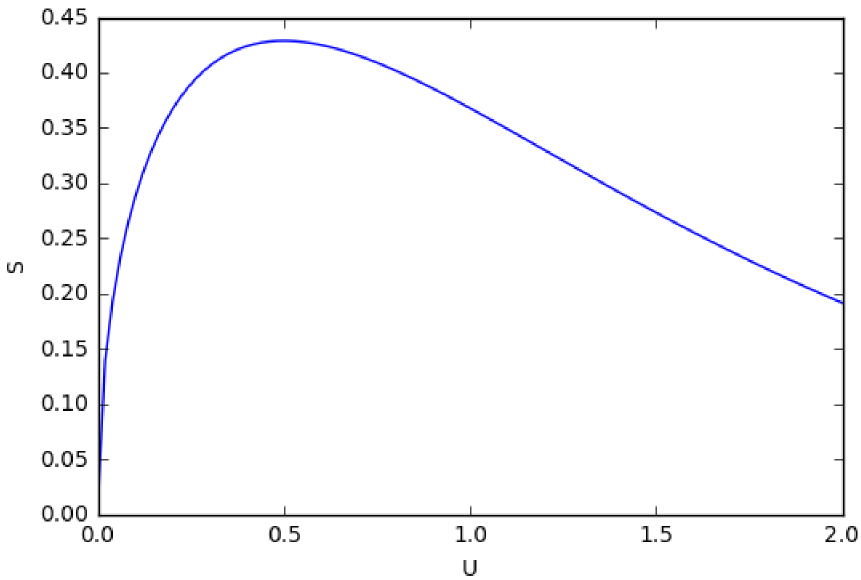
(iii) $\frac{\partial U}{\partial S} = 0,\ as\ S \to 0$

$\therefore$ (8) is not acceptable.

In [64]:
```
import matplotlib.pyplot as plt
import numpy as np

U = np.linspace(0,2,100)
S = []
for u in U:
    s = (u**(0.5)) * np.exp(-u) # assume N = 1 and V = 1
    S.append(s)

plt.plot(U, S,'-')
plt.xlabel('U')
plt.ylabel('S')
plt.show()
```



(9) $U = \left(\frac{NR\theta V}{v_0}\right)\left(1 + \frac{S}{NR}\right)\exp\left(-\frac{S}{NR}\right) = (NV)\left(1 + \frac{S}{N}\right)\exp\left(-\frac{S}{N}\right)$

(i) $U(\lambda S, \lambda V, \lambda N) = \lambda^2\,(NV)\left(1 + \frac{S}{N}\right)\exp\left(-\frac{S}{N}\right) \neq \lambda U(S, V, N)$

(ii) $\frac{\partial S}{\partial U}$ is not monotonically increasing.

(iii) assume $N = 1$ and $V = 1$,

then $\frac{\partial U}{\partial S} = \exp(-S) - \exp(-S)(1 + S)$

thus, $\frac{\partial U}{\partial S} = 0,\ as\ S \to 0$

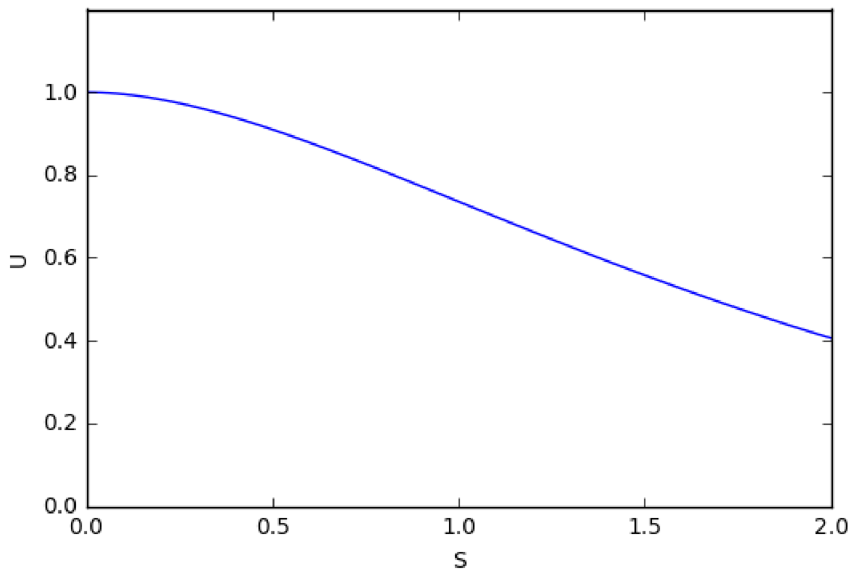
$\therefore$ (9) is not acceptable.

In [2]:

```
import matplotlib.pyplot as plt
import numpy as np

S = np.linspace(0,2,100)
U = []
for s in S:
    u = (1 + s) * np.exp(-s) # assume N = 1 and V = 1
    U.append(u)

plt.plot(S, U,'-')
plt.xlabel('S')
plt.ylabel('U')
plt.xlim(0,2)
plt.ylim(0,1.2)
plt.show()
```



$(10)\ U = \left(\frac{v_0\theta}{R}\right)\frac{S^2}{V}\exp\left(\frac{S}{NR}\right) = \frac{S^2}{V}\exp\left(\frac{S}{N}\right)$

$(i)\ U(\lambda S, \lambda V, \lambda N) = \lambda\frac{S^2}{V}\exp\left(\frac{S}{N}\right) = \lambda U(S, V, N)$

$(ii)\ \frac{\partial S}{\partial U}$ > 0.

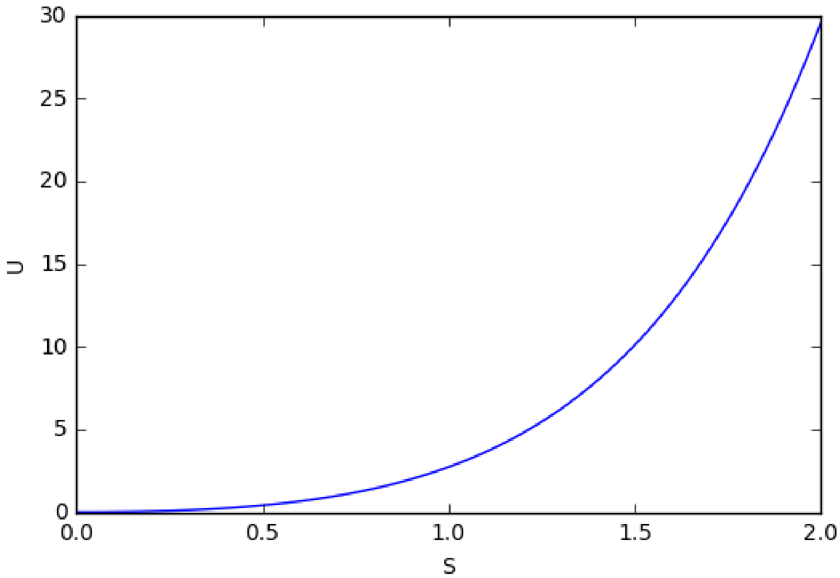
$(iii)\ \frac{\partial U}{\partial S} = 0,\ as\ S \to 0$

$\therefore$ (10) is acceptable.

In [3]:
```
import matplotlib.pyplot as plt
import numpy as np

S = np.linspace(0,2,100)
U = []
for s in S:
    u = (s**(2)) * np.exp(s) # assume N = 1 and V = 1
    U.append(u)

plt.plot(S, U,'-')
plt.xlabel('S')
plt.ylabel('U')
plt.xlim(0,2)
plt.show()
```



Therefore, (2),(4),(6),(8) and (9) are not physically permissible.

Problem 3: Find your equilibrium

The fundamental equations of both systems A and B are

$$S = \left(\frac{R^2}{v_0\theta}\right)^{1/3}(NVU)^{1/3}$$

The volume and mole number of system A are $9 \times 10^{-6}\ m^3$ and 3 mol, respectively, and of system B are $4 \times 10^{-6}\ m^3$ and 2 mol, respectively. First suppose A and B are completely isolated from one another. Plot the total entropy $S_A + S_B$ as function of $U_A/(U_A + U_B)$, where $U_A + U_B = 80$J. If A and B were connected by a diathermal wall and the pair allowed to come to equilibrium, what would U_A and U_B be?

Call

$$X = \frac{U_A}{U_A + U_B}$$

we know $U_A + U_B = 80$, therefore

$$U_A = 80X, \qquad U_B = 80(1 - X)$$

Then setting $R, v_0, \theta = 1$ and plugging in V_A, V_B, N_A and N_B.

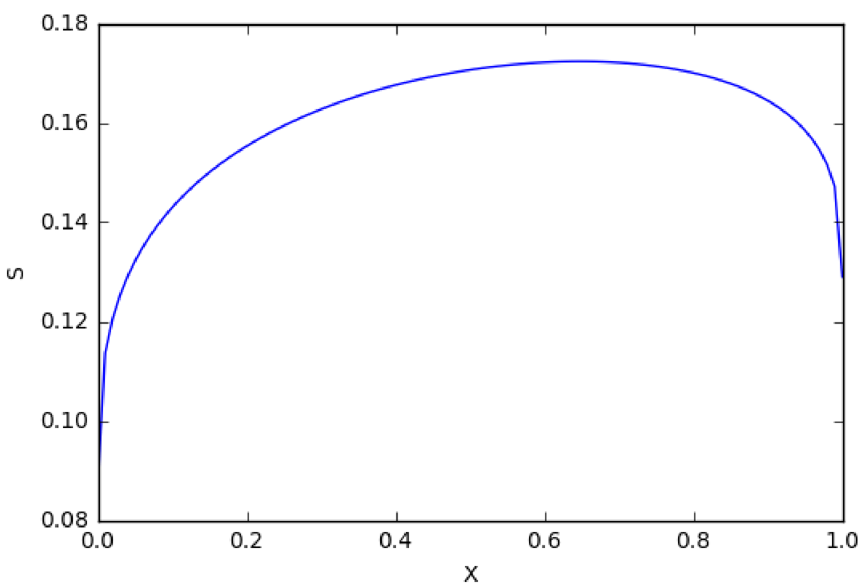
$$S = S_A + S_B = \left(3 \times 9 \times 10^{-6} \times 80X\right)^{1/3} + \left(2 \times 4 \times 10^{-6} \times 80(1 - X)\right)^{1/3} = 0.086(1 - X)^{1/3} + 0.129X^{1/3}$$

Entropy is maximized when $X = 0.65$, which is where we would expect the system to go at equilibrium once the internal wall is made diathermal.

In [96]:
```
import matplotlib.pyplot as plt
import numpy as np

X = np.linspace(0,1,100)
S = []
for x in X:
    s = 0.086 * (1 - x)**(1./3) + 0.129 * (x**(1./3))
    S.append(s)

plt.plot(X, S,'-')
plt.xlabel('X')
plt.ylabel('S')
plt.show()
```



From this graph, S is maximized when $X = 0.65$.

Therefore, $U_A = 80X = 52\ J$ and $U_B = 28\ J$.

An alternative non-graphical method is to solve for where

$$\frac{\partial S}{\partial U} = 0$$

In [108]:
```
from sympy import *
X = Symbol('X', real = True)
S = 0.086 * (1 - X)**(1./3) + 0.129 * (X**(1./3))

Sprime =  S.diff(X) # differentiate S in terms of X

max = solve(Sprime, X) # solve Sprime =0 with respect to X

print 'X =', max[0]
print 'UA =', 80 * max[0]
print 'UB =', 80 * (1 - max[0])
```

```
X = 0.647529554910575
UA = 51.8023643928460
UB = 28.1976356071540
```

Problem 4: Exactly right

The Helmholtz energy A is a thermodynamic state function. Show that

$\left(\frac{\partial A}{\partial V}\right)_T = -P$ and $\left(\frac{\partial A}{\partial T}\right)_V = -S$ implies $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

$$dA = \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT$$
$$\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial V}\right)_T\bigg|_V = \frac{\partial}{\partial V}\left(\frac{\partial A}{\partial T}\right)_V\bigg|_T$$
$$\therefore \frac{\partial(-P)}{\partial T}\bigg|_V = \frac{\partial(-S)}{\partial V}\bigg|_T$$

Problem 5: A difference of degree

Determine whether the following five expressions are homogeneous and, if so, what their degree of homogeneity is:

$(1)\ u = x^2y + xy^2 + 3xyz$

$(2)\ u = \sqrt{x+y}$

$(3)\ u = \frac{x^3+x^2y+y^3}{x^2+xy+y^2}$

$(4)\ u = e^{-y/x}$

$(5)\ u = \frac{x^2+3xy+2y^3}{y^2}$

$(1)\ u(\lambda x, \lambda y, \lambda z) = \lambda^3 \left(x^2 y + x y^2 + 3xyz\right) = \lambda^3 u(x, y, z)$

$\therefore u$ is homogeneous and the degree of homogeneity is 3.

$(2)\ u(\lambda x, \lambda y, \lambda z) = \lambda^{1/2} \sqrt{x + y} = \lambda^{1/2} u(x, y, z)$

$\therefore u$ is homogeneous and the degree of homogeneity is 1/2.

$(3)\ u(\lambda x, \lambda y, \lambda z) = \lambda \frac{x^3 + x^2 y + y^3}{x^2 + xy + y^2} = \lambda u(x, y, z)$

$\therefore u$ is homogeneous and the degree of homogeneity is 1.

$(4)\ u(\lambda x, \lambda y, \lambda z) = e^{-y/x} = u(x, y, z)$

$\therefore u$ is homogeneous and the degree of homogeneity is 0.

$(5)\ u(\lambda x, \lambda y, \lambda z) = \frac{x^2 + 3xy + 2\lambda y^3}{y^2}$

$\therefore u$ is not homogeneous.